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DYNAMIC BEHAVIOR OF VINYL CHLORIDE IN
AQUATIC ECOSYSTEMS

James Hill, IV, et al

Environmental Research Laboratory
Athens, Georgia

January 1976

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by

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ABSTRACT

To evaluate the behavior of vinyl chloride in aquatic ecosystems, best estimate and worst case models of lake and stream ecosystems were analyzed through the use of mathematical simulation. The characteristics of the chemical, biological, and physical transformations of vinyl chloride indicated in the models were determined by laboratory experimentation and extrapolation of reaction data for similar compounds. These transformations included oxidation, substitution, elimination, hydrolysis, and free radical reactions; complexation; direct and indirect photochemical reactions; microbial degradation and toxicity; bacterial, algal, and fungal sorption; and volatilization. Loss of vinyl chloride from the aquatic environment by volatilization appeared to be the most significant process in its distribution.

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SECTION I

CONCLUSIONS AND RECOMMENDATIONS

A worst case system analysis of vinyl chloride behavior in aquatic systems suggests that unrealistically high levels of vinyl chloride inputs would be necessary to maintain significant concentrations in these systems. However, given extreme environmental conditions, aquatic sediments could exhibit long-term storage of low levels of vinyl chloride.

Chemical degradation of vinyl chloride under pH's, reactant concentrations, and temperatures common to the environment should not be significant. Neither auto-oxidation nor degradation by free radicals is important in most natural waters at low vinyl chloride concentrations. Increased persistence of vinyl chloride due to complexation with Ag^+ and Cu^+ should be minimal. Data are not available for consideration of other metal species.

Experiments with distilled water, water from the effluent of a PVC plant, and two natural waters indicate that photolysis of vinyl chloride is probably a slow process under environmental conditions.

Vinyl chloride does not appear to be sorbed by microorganisms, as indicated by laboratory experiments with five mixed bacterial populations, three mixed fungal populations, two axenic bacterial cultures, and one alga. The five mixed bacterial populations did not degrade the vinyl chloride to any detectable extent. Also, at vinyl chloride concentrations up to 900 mg l^{-1} , no toxic effects on the bacterial cultures could be detected.

The rate of bulk exchange of gaseous vinyl chloride between atmosphere and water is about twice that of oxygen. Loss of vinyl chloride by volatilization from water is therefore probably the most significant process in its distribution.

The assumptions and consequently the conclusions of this analysis may be invalid when vinyl chloride enters a receiving water as a component of a tar or sludge or when large concentrations of surface active agents are present with the vinyl chloride in water. Further study is necessary for specific situations where these conditions exist.

The reactions of vinyl chloride with chlorine and hypochlorous acid should be studied under conditions that prevail in the chlorination processes of municipal water treatment plants. Also, the reactions of organics that may form vinyl chloride under these conditions should be studied.

SECTION II

INTRODUCTION

Vinyl chloride ($\text{CH}_2 = \text{CHCl}$), a colorless, highly flammable gas, is used primarily in the production of the resin, polyvinylchloride (PVC). The PVC is then used in the manufacture of many synthetic plastics and rubbers. Vinyl chloride monomer (VCM) is therefore present in many manufacturing operations and, because water is used as a medium in the polymerization reaction, it is also a possible contaminant of waste water discharged from these plants.

In recent studies, chronic exposure to VCM has resulted in liver injury to laboratory rats and rabbits. Also, some workers in PVC plants have contracted angiosarcoma of the liver (1). Because of its possible harmful effects on humans and other living organisms and the ubiquitous nature of vinyl chloride in the manufacturing industry, the behavior of VCM in aquatic ecosystems has come under critical study.

The present study was undertaken to investigate the behavior of vinyl chloride in aquatic systems under conditions simulating large inputs of VCM from industrial sources. The study involved the use of a conceptual model of vinyl chloride interactions in aquatic systems; physical, chemical, and biological experiments with vinyl chloride; mathematical models; and system analysis. The relationships among the various facets of the study are represented in the diagram in Figure 1.

The physical, chemical, and biological interactions of vinyl chloride with the components of aquatic systems determine the behavior of vinyl chloride in the system. The individual interactions can be characterized quantitatively by laboratory experimentation and the behavior of VCM within an aquatic system can be approximated by simulation of a system model. An initial conceptual model of the interactions of vinyl chloride in an aquatic environment, developed as described by Gillett *et al.* (2) is represented by the compartment diagram in Figure 2. In the diagram the boxes represent storage of vinyl chloride or its reaction products and the arrows represent transport or transformation processes.

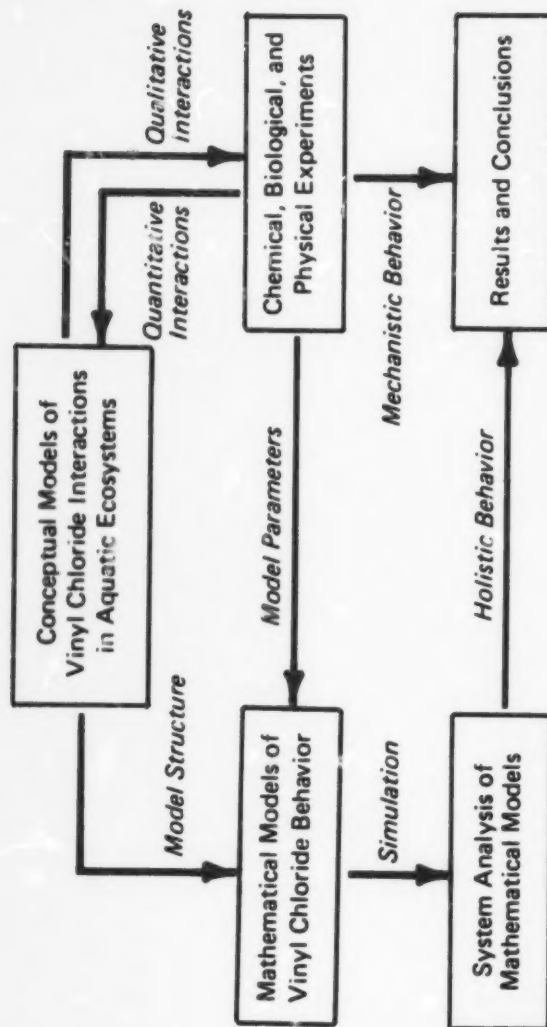


Figure 1. Composite representation of the analysis procedures.

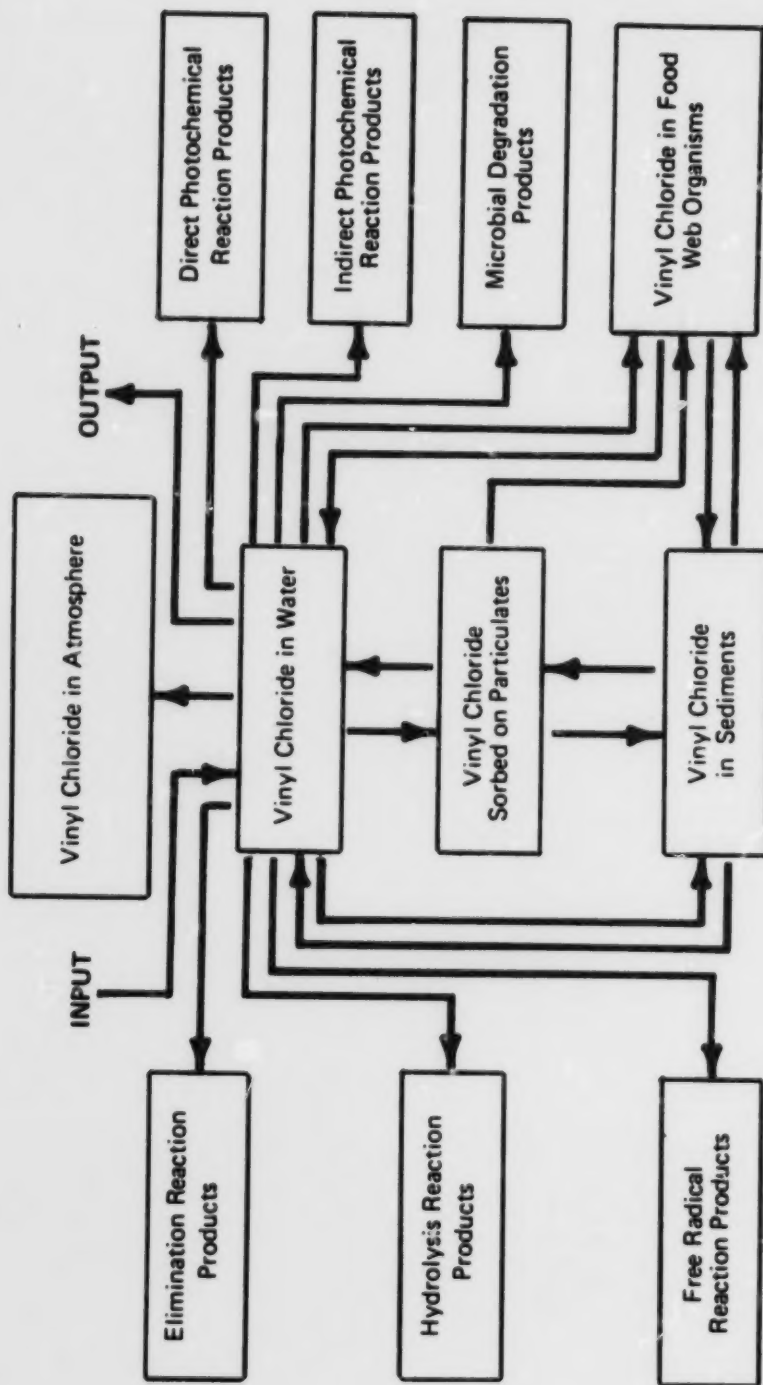


Figure 2. Initial conceptual model of vinyl chloride interactions in an aquatic environment.

A system analysis based upon the conceptual model was used to estimate the behavior of vinyl chloride in aquatic systems under both typical ("best estimate"); and extreme ("worst case") conditions. The rates of the various possible transport and transformation processes were determined in the laboratory.

SECTION III

SYSTEM ANALYSIS

For the purposes of the present study the behavior of vinyl chloride in an aquatic system may be assumed to be a function of four aspects of the system:

- the components of the system with which vinyl chloride may associate or react (e.g., water, organisms, other chemical species);
- the interactions or coupling pathways among these components;
- the characteristics of the interactions (e.g., magnitude, rate, saturation); and
- the rates of vinyl chloride inputs to the system.

The conceptual model of Figure 2 was used to organize the facts and assumptions into an initial system hypothesis as described by Gillett *et al.* (2). This model represents the components and interaction pathways considered to be important in a study of vinyl chloride in an aquatic system. This initial conceptual model was transformed to the conceptual model of Figure 3 through consideration of preliminary studies of vinyl chloride (3), available data on vinyl chloride and analogous compounds, and constraints on the scope of the investigation as defined by the nature of the problem.

The working conceptual model (Figure 3) indicated the need for quantitative characterization of the chemical, biological, and physical interactions between the components. The transport process dynamics have been evaluated in published descriptions of the behavior of the transport media (e.g., particle, fluid, and trophic dynamics). The transformation process dynamics were evaluated by chemical, biological, and physical experimentation.

The qualitative conceptual model (Figure 3) and the associated quantitative interaction descriptions can be logically reduced or expanded to provide a hierarchy of system models. These system models can be represented mathematically and evaluated by simulation to provide descriptions of vinyl chloride behavior at various levels of abstraction or generality.

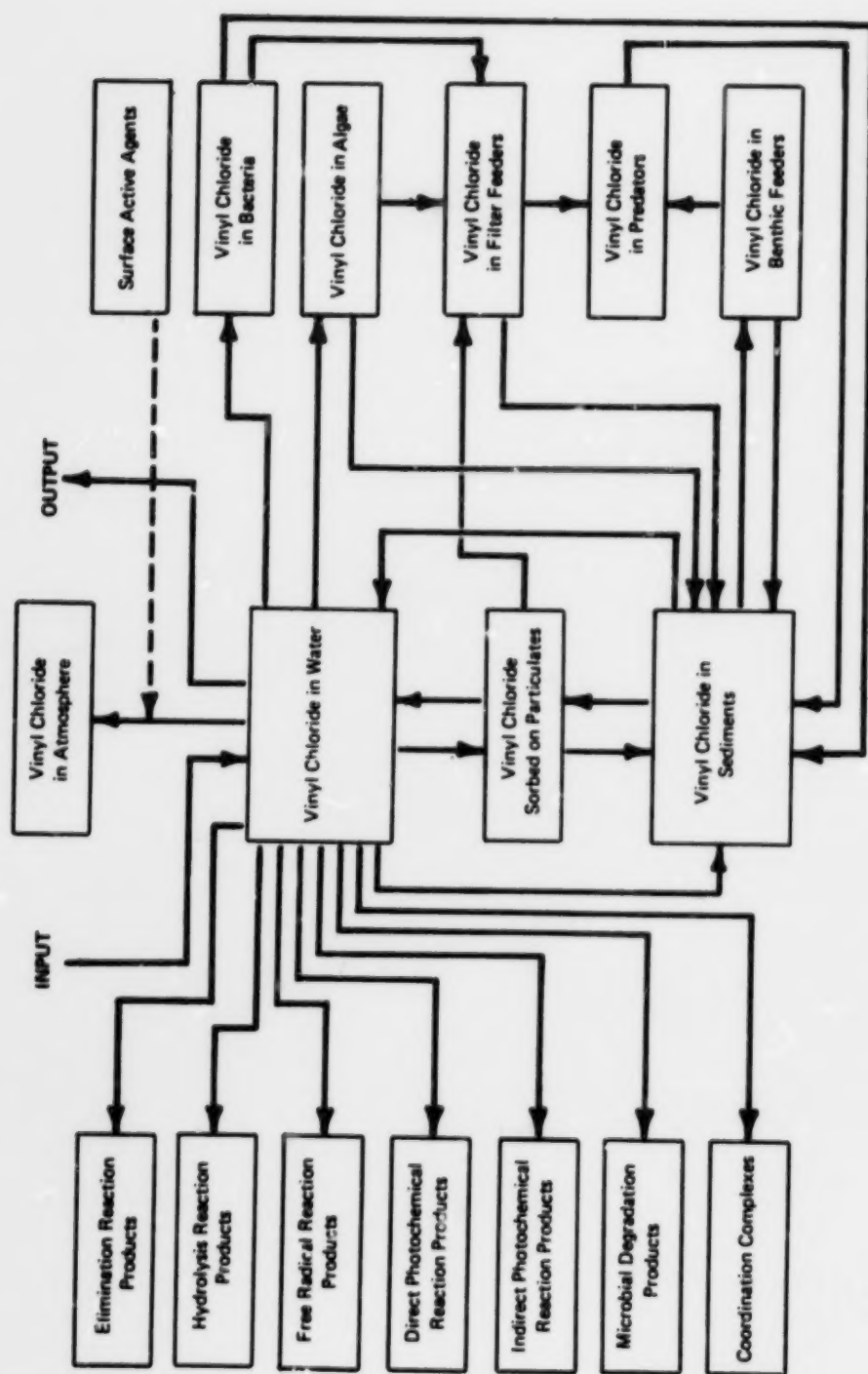


Figure 3. Working conceptual model of vinyl chloride interactions in an aquatic system.

The quantitative aspects of the possible behavior of vinyl chloride in aquatic systems may be approximated by simulation and analysis of a system model of a sample lake and stream. The conclusions resulting from these hypotheses, however, are only as good as the assumptions made in their formulation. These assumptions may be changed to incorporate new information or to apply the analysis to a particular aquatic system.

ASSUMPTIONS

The most significant assumption in this type of analysis is the model itself. The choices of components and their couplings represent a mixture of logical analysis, physical intuition, and personal biases. These choices affect the parameters, inputs, outputs, and responses of the model.

A best estimate approximation of the behavior of vinyl chloride in a sample lake or stream was obtained assuming the most reasonable estimates of the rates of transformation processes as determined from laboratory results. Experiments indicated that rates for all processes except volatilization are essentially zero (Section IV, V, VI, and VII). This assumption results in the simplified model of Figure 4.

To evaluate the boundaries of possible vinyl chloride behavior, two additional system models were derived describing extreme behavior at two levels of resolution. In these worst case analyses, all chemical and biological transformation processes were assumed to proceed at a rate that is just below the level of measurement in the experimental procedures used for their determination. Conditions in the aquatic environment (e.g., turbulence, stratification, sediment scouring) were assumed to be at the extreme of the environmentally realistic range that would cause worst case system responses. The system models of Figures 5 and 6 were analyzed subject to these worst case assumptions.

A set of linear, first-order ordinary differential equations was assumed to be a reasonable mathematical approximation of the dynamic behavior of vinyl chloride in the hypothesized structures. This is justified by recourse to the theory of linearization about an operating path (4) and assumes that vinyl chloride input represents a small system perturbation.

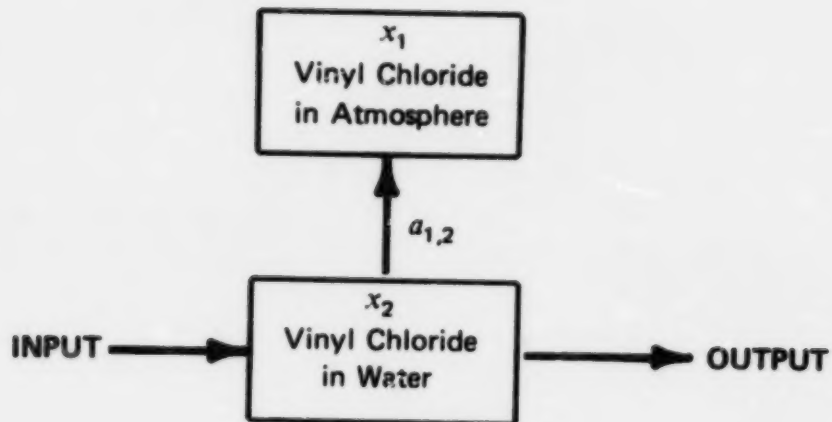


Figure 4. Best estimate model of vinyl chloride in the aquatic environment.

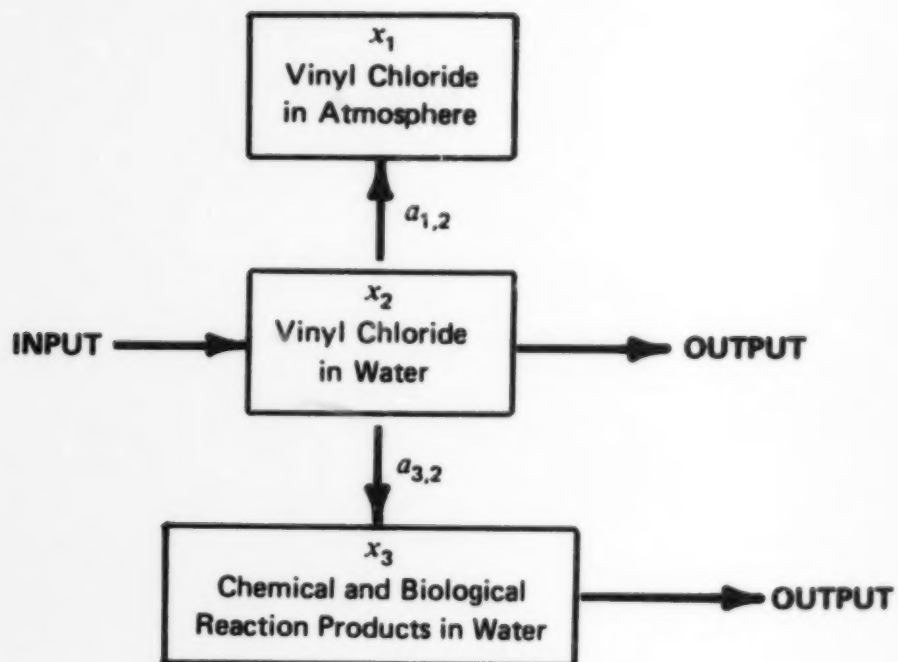


Figure 5. System model with worst case chemical and biological transformation reaction rates.

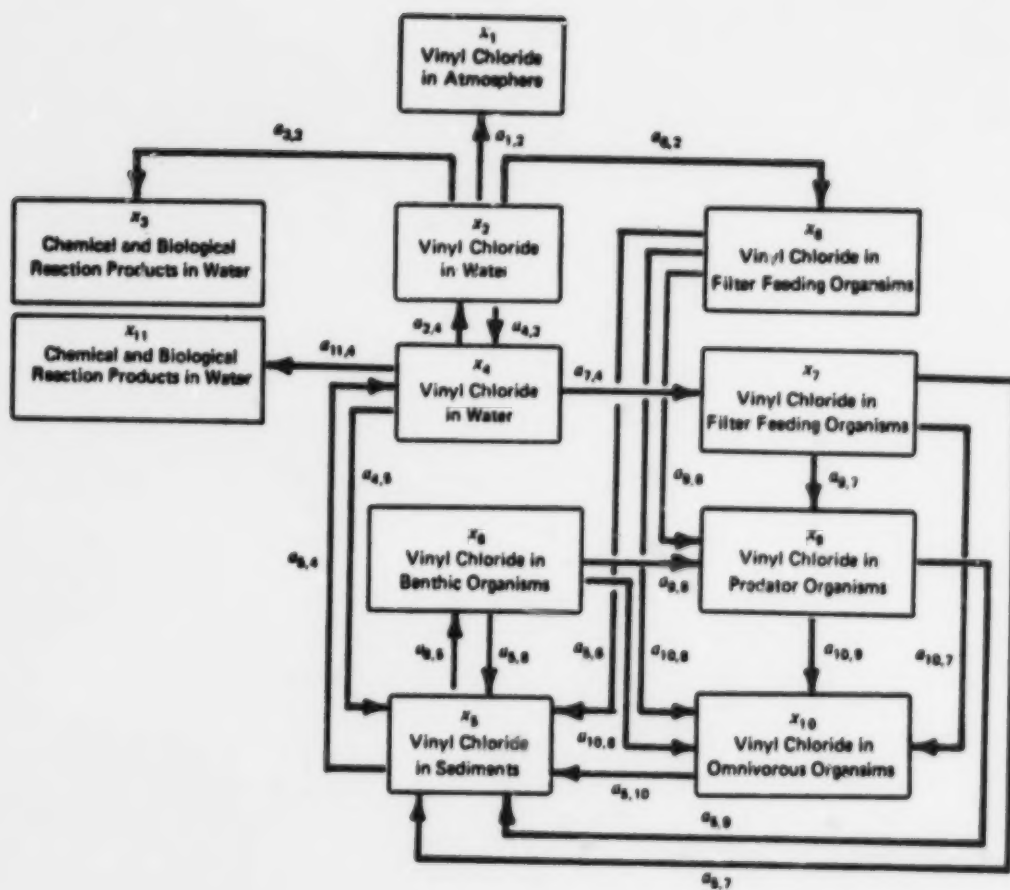


Figure 6. System model of vinyl chloride in stratified lake with a simple idealized food web.

The system diagrams of Figures 4 through 6 therefore were directly translated to a set of equations that can be written in vector form as

$$\frac{dX}{dt} = AX + BU \quad (1)$$

where the x_i represent the variable quantities stored in the boxes; the a_{ij} represent the rate coefficients for transfer from box j to box i ; and the u_i represent the inputs to box i .

The typical or sample lake is assumed to be 10^4 m^2 and 10 m deep. It has a residence time of 10 days and stratifies in summer with a metalimnion 0.5 m wide centered at a 5-meter depth. It is completely mixed above and below the thermocline when stratified and completely mixed otherwise. The typical or sample stream parameters were derived from Tsivoglou and Wallace's (5) data on the Chattahoochee and Jackson rivers.

For the best estimate model, equation (1) reduces to

$$\frac{dx_2}{dt} = a_{1,2} x_1 + u_1 \quad (2)$$

The rate coefficient value, $a_{1,2}$, of the best estimate model of the lake is a bulk gas exchange coefficient between water and atmosphere of 0.436 day^{-1} (6, Section VII of this report). The input was set at 1 mg l^{-1} vinyl chloride in the influent water as a reference value.

The gas exchange coefficient, $a_{1,2}$, in the best estimate stream model is 0.96 day^{-1} (5, Section VI of this report), and the input is again 1 mg l^{-1} vinyl chloride.

The worst case model was analyzed using values for a_{ij} listed in Table 1. It should be noted that these are extreme values and would not be expected to apply in a typical lake or stream. The values for each of the coefficients were chosen as described.

- $a_{1,2}$ -- as discussed for best estimate model.
- $a_{3,2}$ and $a_{11,4}$ -- represent the combined effects of the hypothesized chemical and biological reaction pathways for vinyl chloride in water. Values were determined either by assuming that the reaction occurred at a rate immediately below the level of detection or by extrapolating laboratory conditions to their extreme analog in the aquatic environment.
- $a_{4,2}$ and $a_{2,4}$ -- are the results of an approximation for eddy current transport across a thermocline, which was extrapolated to the hypothetical lake morphology (7).
- $a_{6,2}$, $a_{7,4}$, and $a_{8,5}$ -- were based upon the fraction of the lower trophic level biomass assumed to be assimilated per year (8).
- $a_{9,6}$, $a_{9,7}$, and $a_{9,8}$ -- were based on the trophic level assumption used for $a_{6,2}$, $a_{7,4}$, and $a_{8,5}$ and the assumption of an evenly distributed food preference.
- $a_{10,6}$, $a_{10,7}$, and $a_{10,8}$ -- were based on the trophic level assumption used for $a_{6,2}$, $a_{7,4}$, and $a_{8,5}$ and an evenly distributed food preference.
- $a_{5,6}$, $a_{5,7}$, $a_{5,8}$, and $a_{5,9}$ -- were based upon an average 10-day turnover time and a population loss of 90% of ingested material averaged over a year (8).
- $a_{5,4}$ -- assumes an average settling rate for particulates of 0.1 cm sec^{-1} (7) and diffusion-limited transport in unmixed interstitial waters with an effective surface fraction of 0.38 for several sizes of closely-packed spheres. The diffusion coefficient for vinyl chloride was estimated from the diffusion coefficient for oxygen and the ratio of gas exchange coefficients (9).
- $a_{4,5}$ -- assumes diffusion limited transport and no scouring of sediments.

The sorption of vinyl chloride onto particulates was assumed to be reversible and very fast so that an equilibrium with a $K = 10$ (see Section VI) was maintained. The concentration of organic particulates was taken as constant (i.e., input = output) at 1.66 mg l^{-1} (7).

Table 1. WORST CASE MODEL PARAMETERS

Symbol	Interactions	Value (day ⁻¹)
a _{1,2}	Volatilization of vinyl chloride	0.436
a _{3,2}	Chemical and biological degradation	0.115
a _{11,4}	Chemical and biological degradation	0.115
a _{2,4}	Transport across thermocline	0.0178
a _{4,2}	Transport across thermocline	0.0178
a _{6,2}	Uptake by filter feeding organisms	0.000292
a _{7,4}	Uptake by filter feeding organisms	0.000292
a _{8,5}	Uptake by benthic organisms	0.000292
a _{9,6} ; a _{9,7} a _{9,8}	Uptake by predator	9.73 (10 ⁻⁵)
a _{10,6} ; a _{10,7} a _{10,8} ; a _{10,9}	Uptake by omnivore	7.3 (10 ⁻⁵)
a _{5,6} ; a _{5,7} a _{5,8} ; a _{5,9}	Turnover rate of organisms	0.1
a _{5,4}	Water to sediment transport	0.107 (10 ⁻²)
a _{4,5}	Sediment to water transport	3.45 (10 ⁻⁴)
a _{1,1}	Loss from compartment	$\sum_j a_{j1}$
u ₂	Input to water	1 ppm
u ₄	Input to water	1 ppm

Complexation of vinyl chloride with silver or copper was assumed to be negligible since typical Cu^+ and Ag^+ concentrations in aquatic systems are less than 30 mg m^{-3} , as much as 80% of which is adsorbed onto organic colloids (7). In addition, complexation would probably be very rapid and reversible. Finally, the concentration of vinyl chloride in the air above the water was assumed to be maintained at essentially zero by surface replacement.

RESULTS AND DISCUSSION

The concentration of vinyl chloride in the water and the cumulative loss to the air for the best estimate model (Figure 4) of the sample lake are shown in Figure 7. These results are for a vinyl chloride input of 1 mg l^{-1} and a fractional input of 10% of the total water volume. A similar result for a volume of water in the sample stream as it travels downstream is indicated in Figure 8. These results indicate that with a volume input of 10% water per day containing 1 mg l^{-1} vinyl chloride, the concentration of vinyl chloride in the sample stream and lake would be less than 0.2 mg l^{-1} .

If the chemical and biological reaction pathways with worst case rates are added to the preceding examples (Figure 5), the resultant distribution of vinyl chloride is as indicated in Figures 9 and 10. It should be noted that in this worst case no losses of degradation products other than washout or dilution are postulated. Even so, the degradation products reach a steady-state concentration below 0.3 mg l^{-1} .

The behavior of vinyl chloride in the worst case model of Figure 6, which represents a stratified lake with a simplistic food web, is indicated in the graphs of Figures 11 through 14. The results are self-explanatory except for the concentrations in sediments and benthic organisms. The assumptions of diffusion-limited exchange between water and unmixed lower sediment layers and of lack of scour dictate a relatively long half-life for vinyl chloride in the sediment-benthic organism-predator-omnivore cycle ($t_{1/2} \approx 3 \text{ yr}$). With these assumptions the vinyl chloride concentration in the sediment approaches a steady-state value of 0.358 mg l^{-1} in about 15 years. The vinyl chloride in benthic organisms reaches a steady-state value of 0.013 mg l^{-1} in the same time period while the concentrations in other organisms are less.

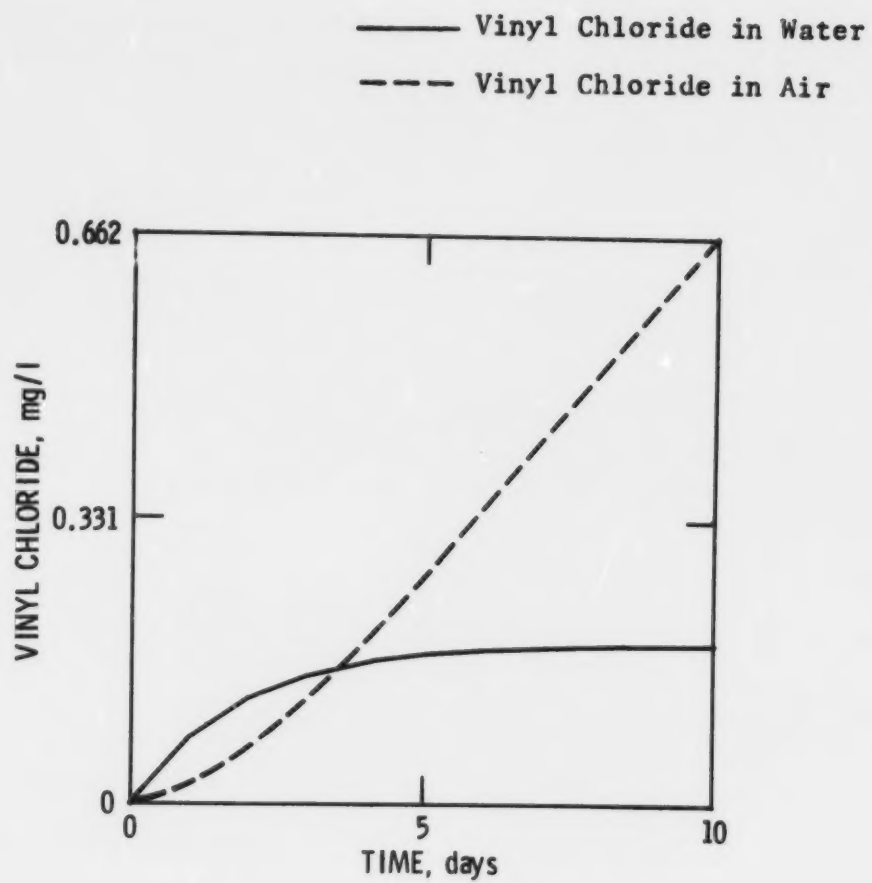


Figure 7. Lake simulation with best estimate model.

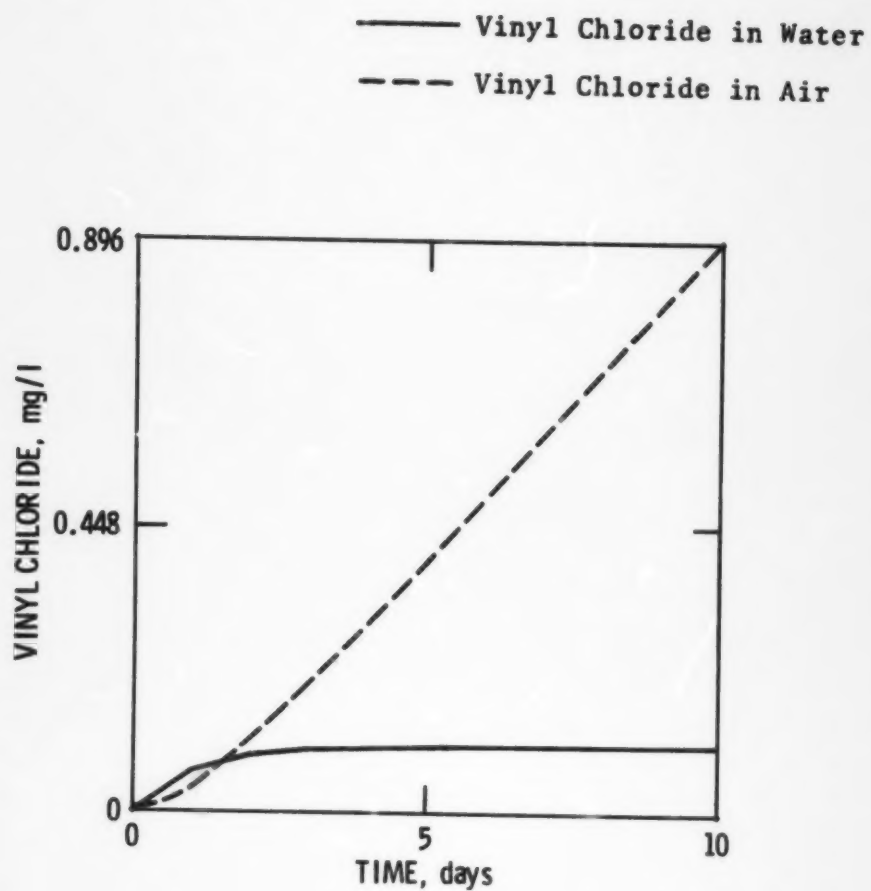


Figure 8. Stream simulation with best estimate model.

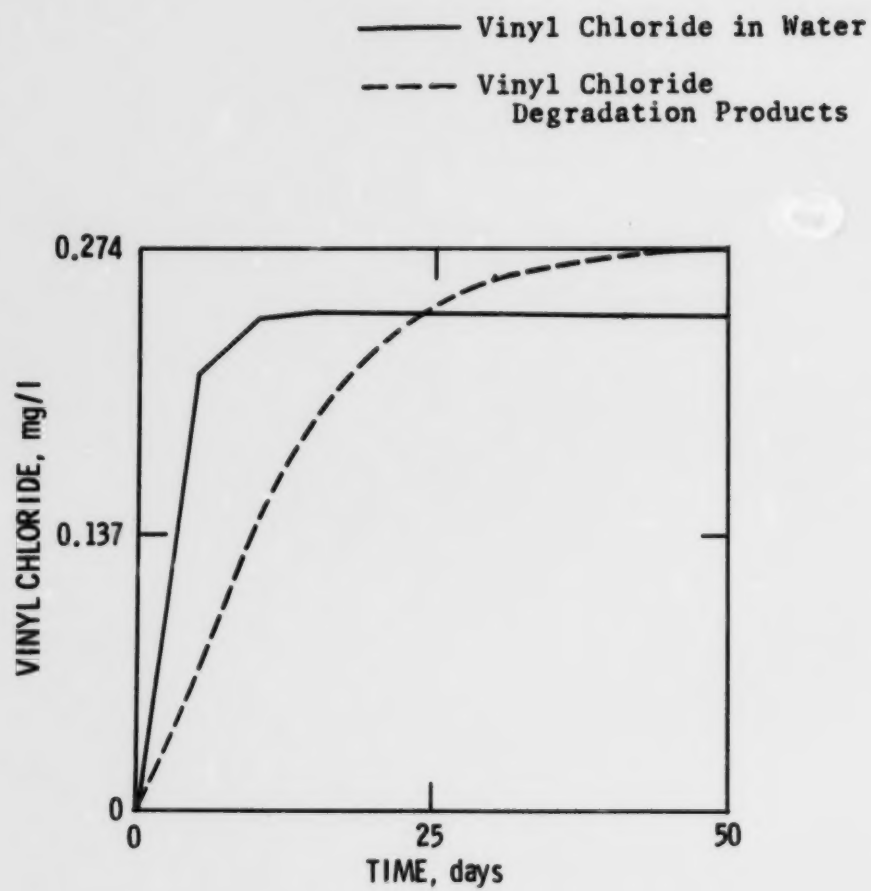


Figure 9. Lake simulation of the model of Figure 5.

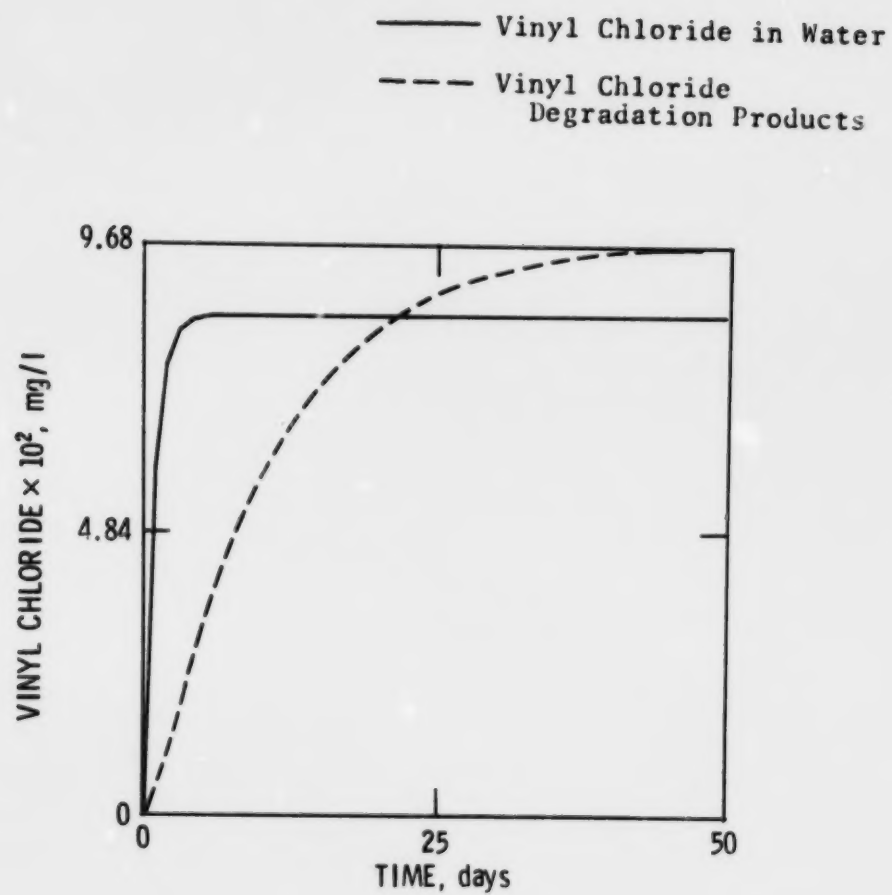


Figure 10. Stream simulation of the model of Figure 5.

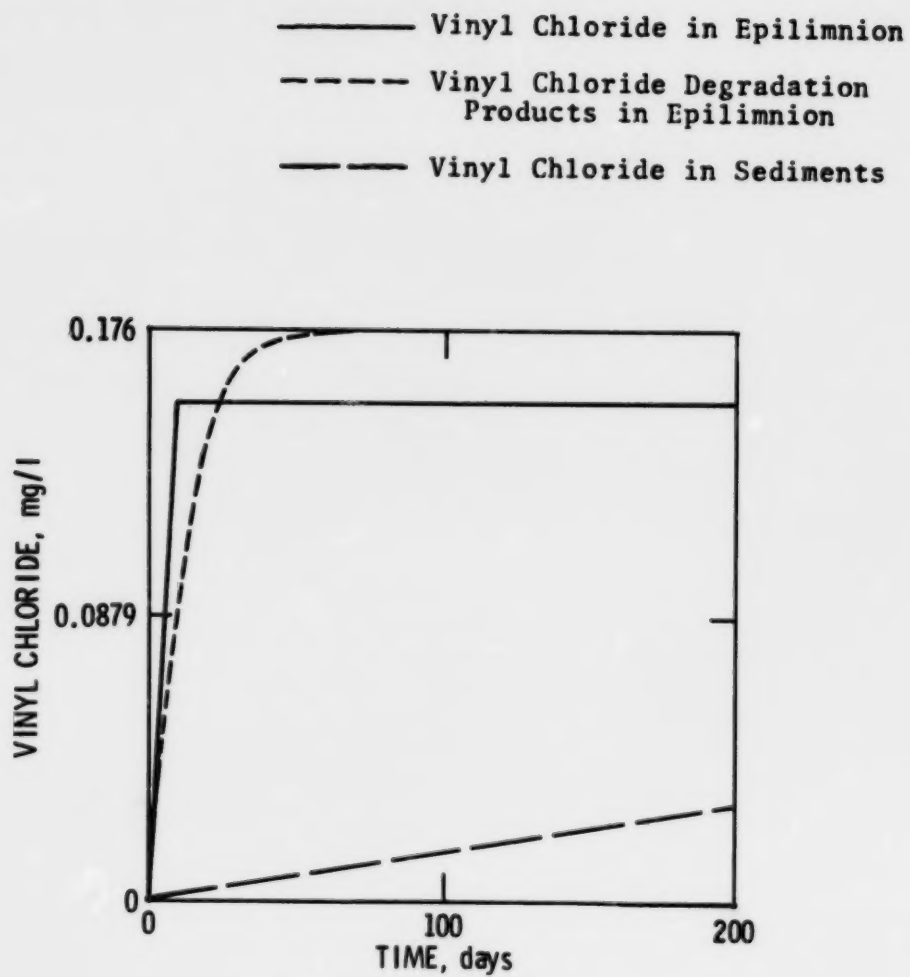


Figure 11. Stratified lake simulation of the model in Figure 6.

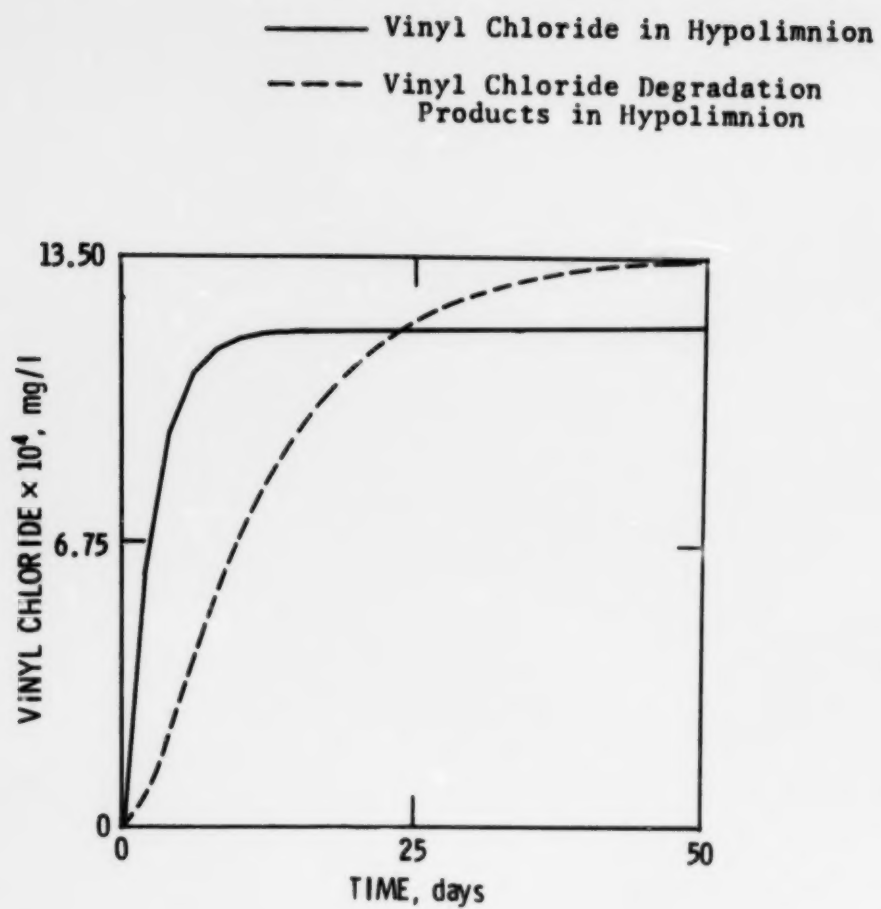


Figure 12. Stratified lake simulation of the model in Figure 6.

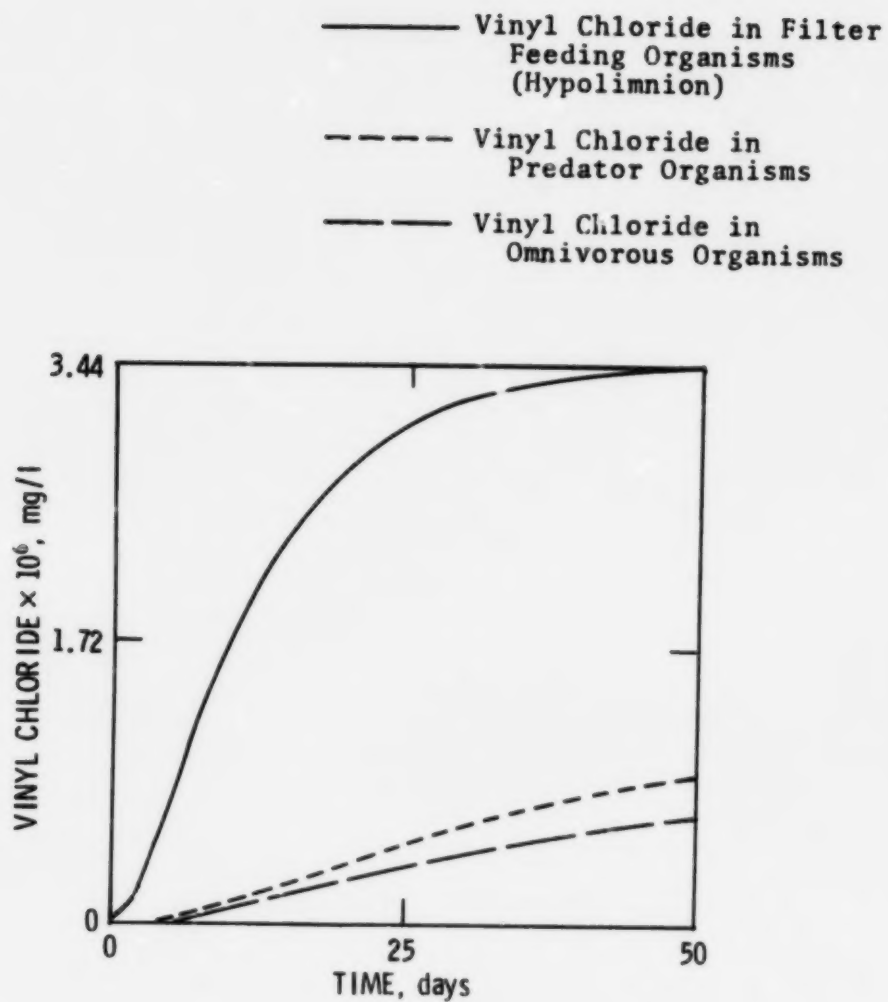


Figure 13. Stratified lake simulation of the model in Figure 6.

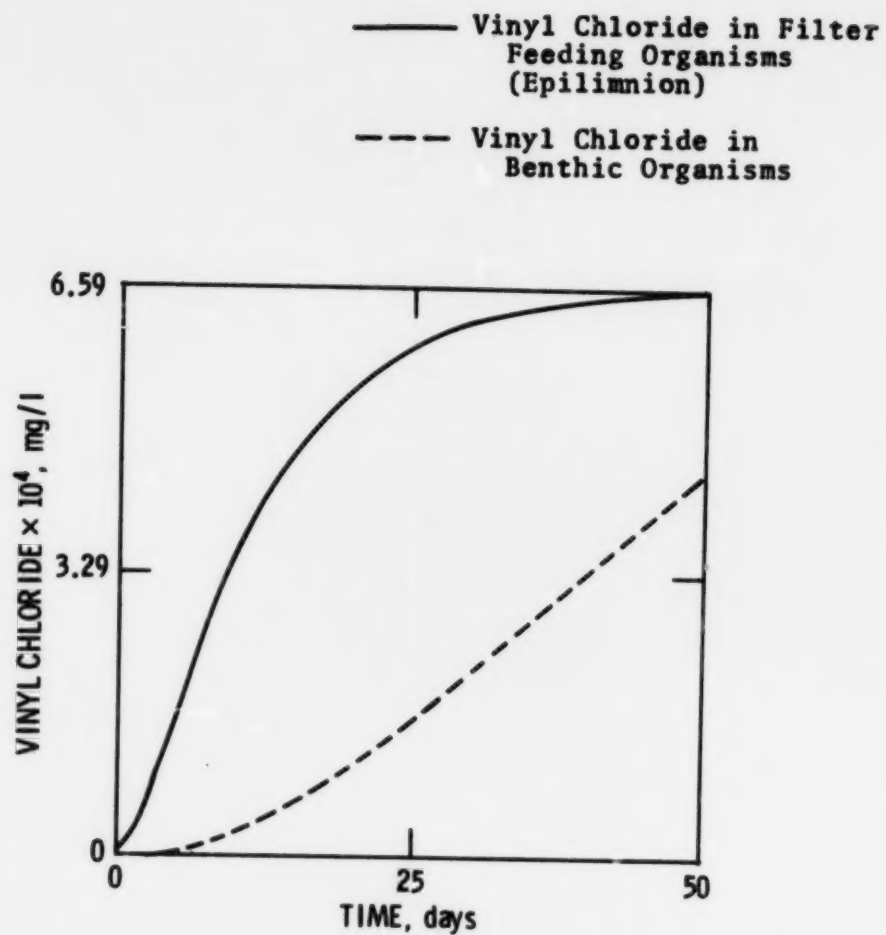


Figure 14. Stratified lake simulation of the model in Figure 6.

A diagnostic input consisting of a pulse of vinyl chloride can produce a characteristic response for each component. This response is a very concise way of demonstrating the behavior predicted by the system hypothesis. The total response to a pulse input contains all the information necessary to characterize the system (10). Figures 15 through 17 show the component responses to a pulse input of 1 mg l^{-1} vinyl chloride to the epilimnion waters for the model of Figure 6. In Figure 18, the beginning of the slow loss of vinyl chloride from the sediments can be seen after about 60 days.

The results of a pulse input of 1 mg l^{-1} vinyl chloride to the sediments are shown in Figures 19 through 21. The slow but continuous loss of vinyl chloride from the sediments is evident. This loss occurs to the air (rate $\pm 7 \times 10^{-6} \text{ mg l}^{-1} \text{ day}^{-1}$) and to downstream waters (rate $\pm 3.9 \times 10^{-6} \text{ mg l}^{-1} \text{ day}^{-1}$).

All of the results assume steady-state levels of biomass components and particulates and do not include any low level toxic effects or biomagnification (i.e., selective retention of vinyl chloride). From the results of these model simulations it appears that vinyl chloride should not remain in an aquatic ecosystem under most natural conditions.

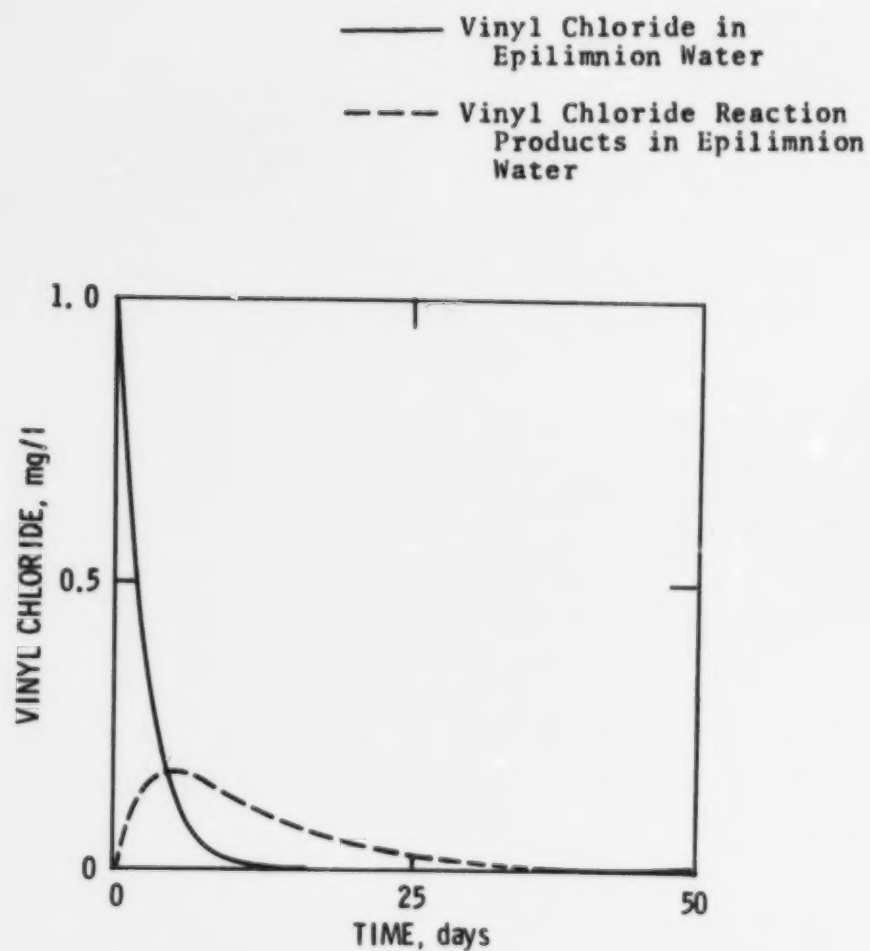


Figure 15. Stratified lake model's response to pulse input of vinyl chloride to epilimnion water.

- Vinyl Chloride in Filter Feeding Organisms (Hypolimnion)
- Vinyl Chloride in Benthic Organisms
- - - - Vinyl Chloride in Predator Organisms
- Vinyl Chloride in Omnivorous Organisms

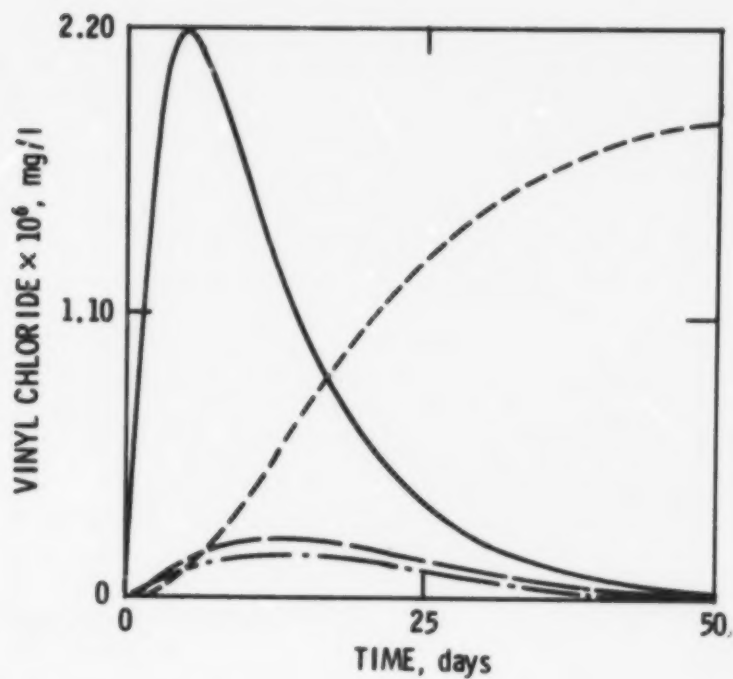


Figure 16. Stratified lake model's response to pulse input of vinyl chloride to epilimnion water.

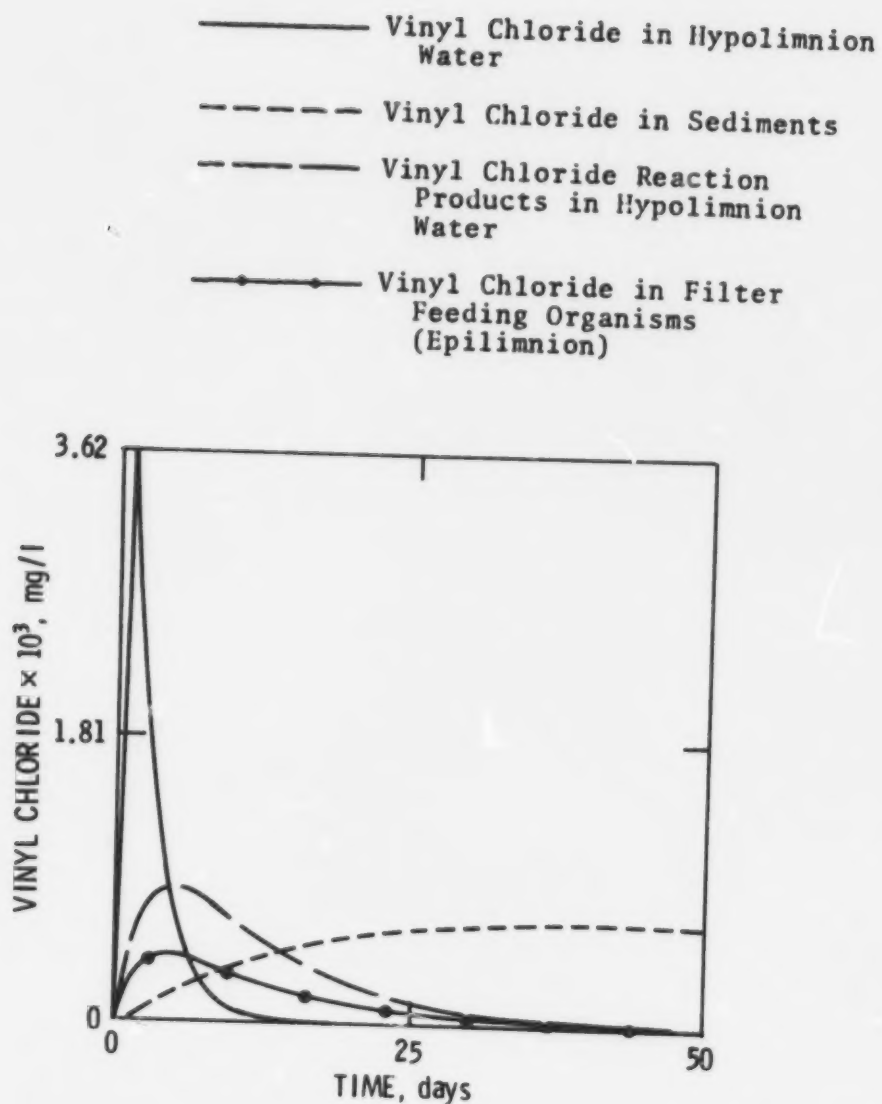


Figure 17. Stratified lake model's response to pulse input of vinyl chloride to epilimnion water.

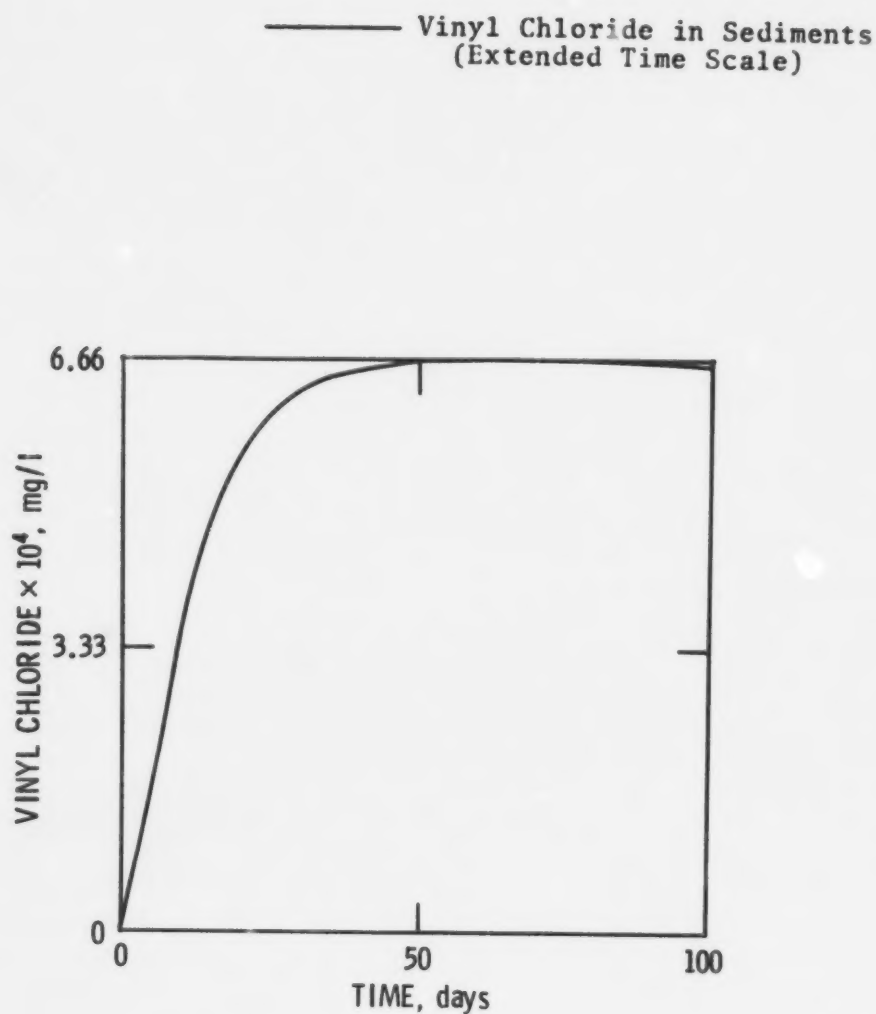


Figure 18. Stratified lake model's response to pulse input of vinyl chloride to epilimnion water.

— Vinyl Chloride in Sediments

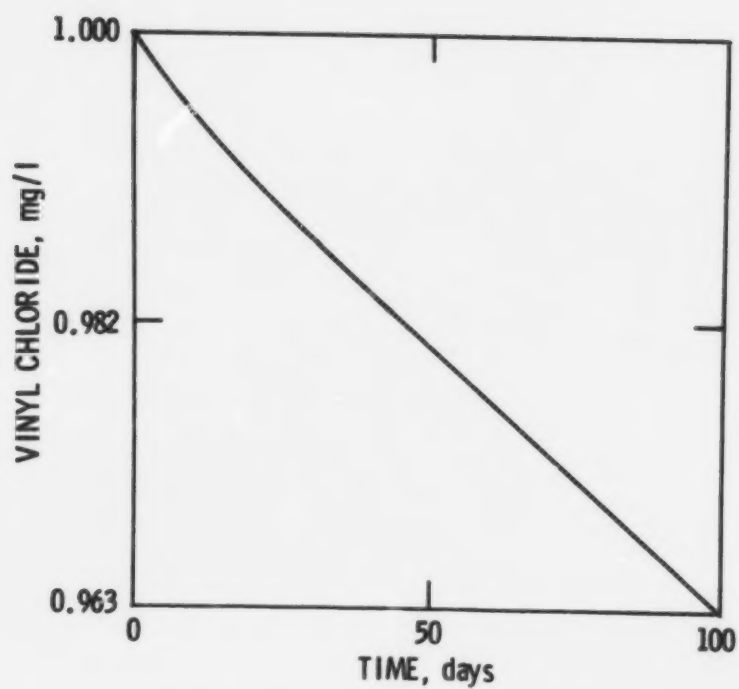


Figure 19. Stratified lake model's response to pulse input of vinyl chloride to sediments.

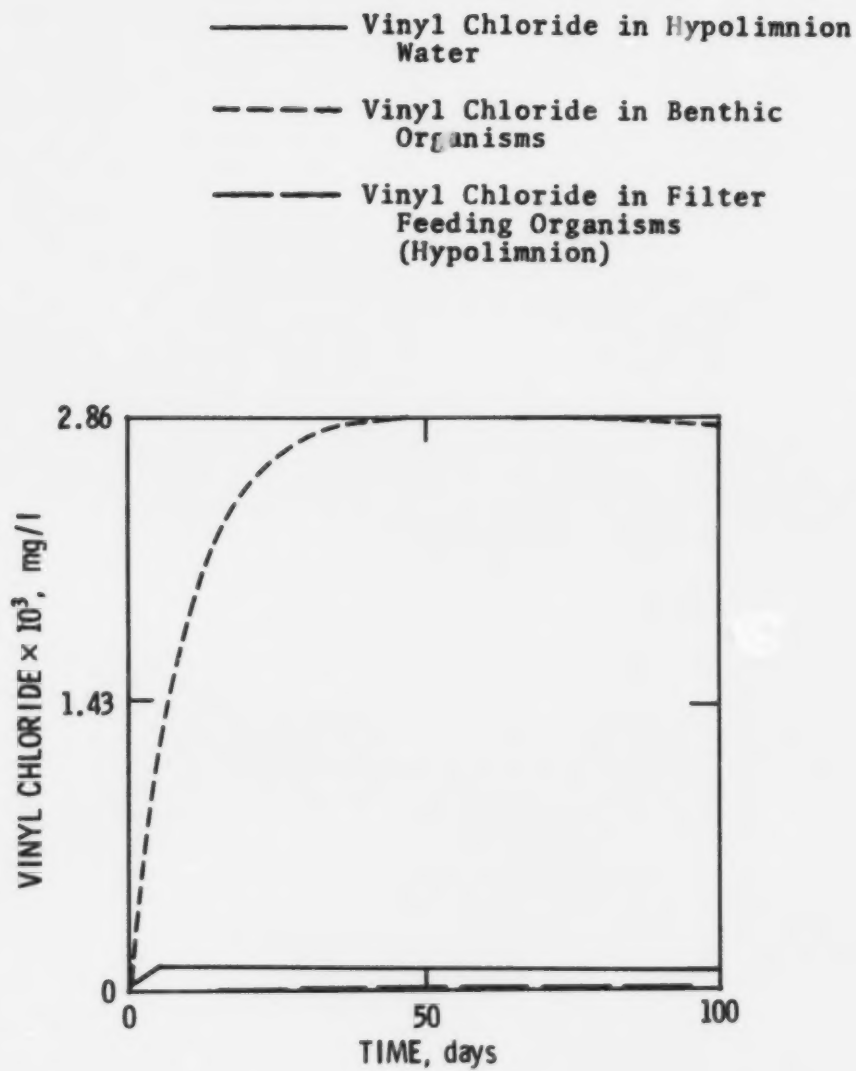


Figure 20. Stratified lake model's response to pulse input of vinyl chloride to sediments.

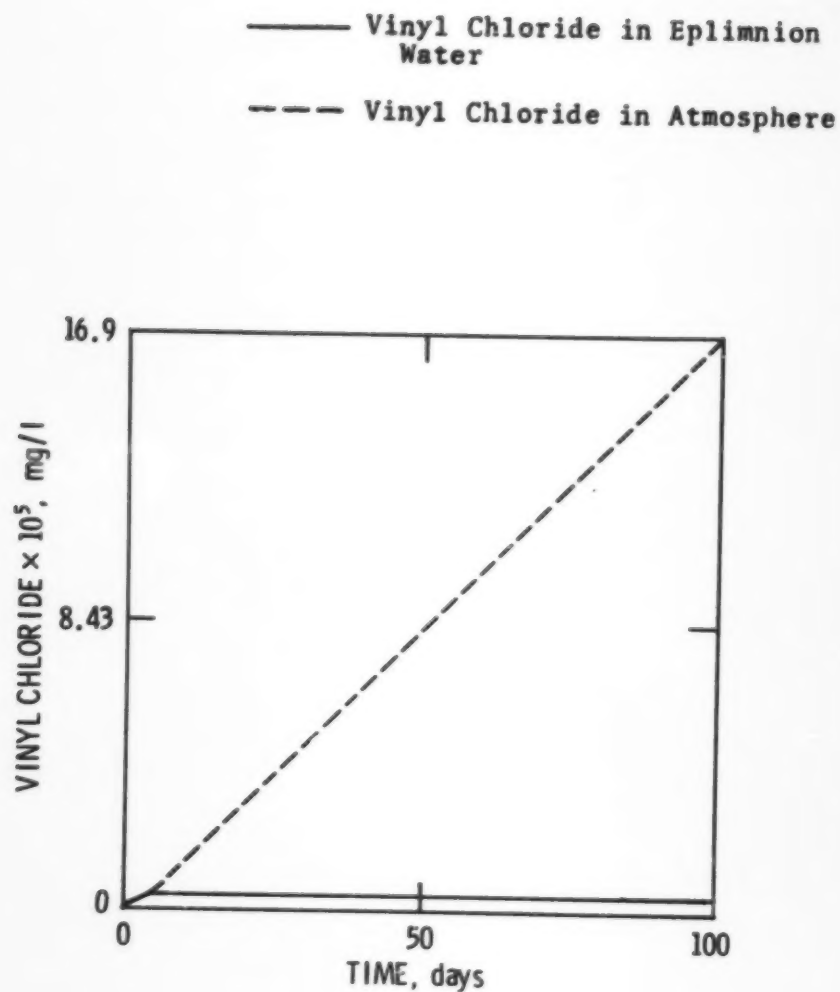


Figure 21. Stratified lake model's response to pulse input of vinyl chloride to sediments.

SECTION IV

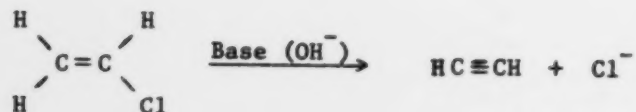
CHEMICAL INTERACTIONS

No reference to studies of the degradation of vinyl chloride in water could be found in the literature. However, considerable data are available concerning the chemistry of vinyl chloride and related compounds that can be extrapolated to reaction conditions anticipated in the environment. Evidence supporting such extrapolations was obtained in a few preliminary experiments.

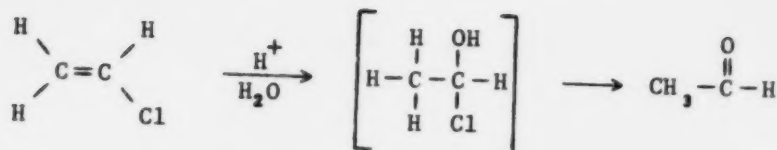
Four pathways were postulated as potential mechanisms for chemical degradation or alteration of vinyl chloride in the environment: substitution (11), elimination (12), addition (13), and oxidation (14).

In nucleophilic substitution, the chloride ion is displaced by a nucleophilic species (Nu) (11). Reactive nucleophiles common to the aquatic environment are amines, thiols, water, and hydroxide ion. The reaction can be either first or second order depending on the specific mechanism.

The most probable elimination reaction in the environment is one in which hydrogen chloride is eliminated from vinyl chloride in the presence of base, producing acetylene (12). This is a second-order reaction and the rate is dependent upon the concentrations of both vinyl chloride and base. The most significant base present in natural water would be hydroxide ion:



The addition reaction most likely to occur to vinyl chloride in the aquatic environment is the addition of water across the carbon-carbon double bond, catalyzed by acid (13).



This reaction is second order with its rate dependent upon concentrations of both vinyl chloride and acid.

Based on kinetic studies in mixed systems, only a few oxidative processes are potentially important for vinyl chloride in the environment (14). Autooxidation (with molecular oxygen) (16) is a possibility; but since its rate is dependent upon the rate of homolytic cleavage of the strong carbon-hydrogen bond, the rate of oxidation of vinyl chloride would be slow.

Free radicals are anticipated to react with the carbon-carbon double bond (14), resulting in oxidation. However, since literature data are not available to evaluate the role of free radicals in natural waters, extrapolation of laboratory data to natural waters is tenuous.

The reactivity of vinyl chloride was studied, and known structure-reactivity relationships and activation parameters were used to evaluate the significance of the above pathways for vinyl chloride disappearance in the environment.

MATERIALS AND METHODS

Vinyl chloride was obtained from Matheson Chemical Company and used as received. Distilled water was used in all experiments except for natural water studies. The Oconee River water sample was obtained in Athens, Georgia, and filtered through a 0.22- μ filter prior to use (pH 6.1). The Okefenokee Swamp water sample was obtained at Kingfisher Landing, Okefenokee Swamp, Georgia, and was used as obtained (pH 4.2). Hydrogen peroxide was purchased from Baker Chemical Company.

A special reaction vessel (Figure 22) designed to eliminate volatilization, was made for these studies.

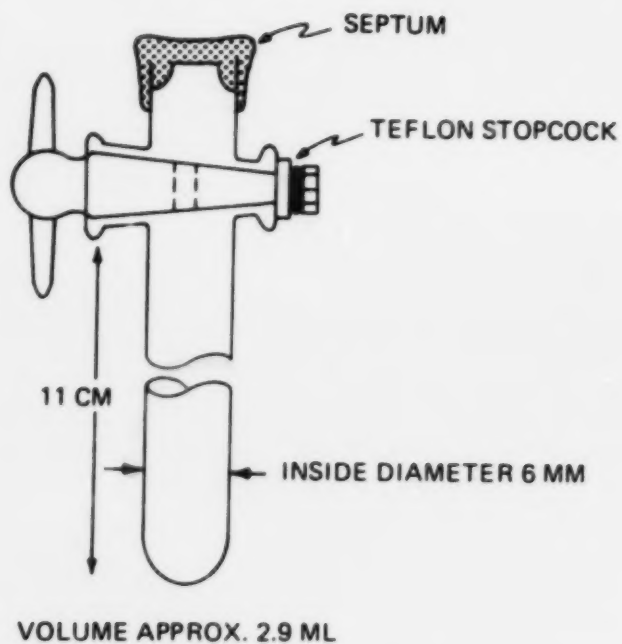


Figure 22. Vinyl chloride reaction vessel.

The vessel was filled to the top with water and 20 ml of vinyl chloride was added. The filled vessel was placed in a constant temperature bath ($\pm 2^\circ\text{C}$) and removed at recorded intervals for analysis. The concentration of vinyl chloride at each time interval was determined by comparison of glc peak heights using a vinyl chloride-carbon tetrachloride standard solution. Experimental error was determined to be $\pm 10\%$.

Glc analysis was carried out on a Tracor Microtech 220 Gas Chromatograph fitted with a 3 m x 0.63 cm column packed with 0.4% Carbowax 1500 on Carbopack; injection, column, and detector temperatures were 210°C , 40°C , and 210°C , respectively.

RESULTS AND DISCUSSION

pH Studies

In reaction mixtures at pH 3.0 (HCl), 7.0, and 11.0 (NaOH) at 85°C , no reaction could be detected after 27 hours. Extrapolation of data, assuming hydrolysis, elimination, addition, or substitution mechanisms, indicates that these reactions would have half-lives on the order of years.

Literature information was used to estimate half-lives for several possible reactions of vinyl chloride under environmental reaction conditions (Table 2). The estimated half-lives were in good agreement with our experimental data. In view of these half-lives, any contribution to the disappearance of vinyl chloride by chemical degradation via these pathways normally would not be significant since other processes are faster.

In environments like municipal water chlorination facilities, however, high concentrations of chlorine would exist. Based on the reactivity of carbon-carbon double bonds with chlorine and hypochlorous acid, under such conditions vinyl chloride may be converted to more highly chlorinated compounds.

Oxidation Studies

The reactivity of vinyl chloride with molecular oxygen was also investigated. Experiments were carried out at 20

Table 2. ORDER OF MAGNITUDE ESTIMATES FOR HALF-LIVES
FOR VINYL CHLORIDE REACTIONS

Reaction	Literature data			Estimated $t_{1/2}$ at 25°C ^g
	Temp. (°C)	Reactant	Maximum rate constant M ⁻¹ sec ⁻¹	
Elimination ^a	95.53	Methoxide	10 ⁻⁷	<10 yr
Substitution ^b	130	C ₂ H ₅ S ⁻	10 ⁻⁹	<10 yr
Addition ^c	25	H ₂ O	10 ⁻⁶	<1 yr
Addition ^d	25	Cl ₂	10 ⁻¹	140 hr
Addition ^e	25	HOCl	10 ⁻²	1000 hr
Hydrolysis ^f	120	H ₂ O	No RX	<10 yr

^aReference 17, methanol solvent, 10⁻³M methoxide.

^bReference 18, reaction of 1-chloropropene in ethanol at 1×10^{-3} M thiol.

^cReference 19, acid catalyzed hydration at pH 3.

^dReference 20, 1,3,3-trichloropropene in aqueous acetic acid---1 mg l⁻¹ chlorine.

^eReference 21, hypohalous acid addition to allyl alcohol at pH 4.5---1 mg l⁻¹ hypohalous acid.

^fReference 15.

^gCalculated assuming pseudo first-order kinetics.

mg l⁻¹ vinyl chloride in water saturated with molecular oxygen at elevated temperatures. After 12 hours at 85°C, no degradation of the vinyl chloride could be detected. At temperatures and oxygen concentrations in natural waters, therefore, vinyl chloride will not be degraded by molecular oxygen at a significant rate.

As anticipated, at elevated temperatures vinyl chloride was degraded by hydrogen peroxide. At 85°C hydrogen peroxide decomposes to give hydroxy radicals (HO•), which react with vinyl chloride. With 1×10^{-2} M hydrogen peroxide and 1×10^{-4} M vinyl chloride, the reaction obeys zero-order kinetics, indicating that decomposition of hydrogen peroxide is the rate-determining step.

The significance of this reaction pathway is difficult to assess because no data are available concerning the concentration and species of free radicals in natural waters. These experiments do indicate that if reactive radicals were present in natural waters at significant concentrations, they may potentially degrade vinyl chloride.

Natural Waters

Vinyl chloride was shown to be chemically stable in two natural water samples. No degradation could be detected in Oconee River water (pH 6.1) and Okefenokee Swamp water (pH 4.2) after 41 hours at room temperature and at 85°C. Assuming the pathways previously discussed, extrapolation of the elevated temperature data to environmental conditions would indicate a minimum half-life of at least one year. Although only two representative water samples were employed, the results obtained are in agreement with behavior predicted based on known chemical reactivity of vinyl chloride.

Complexation

To study the effect of complexation with metal ions on the persistence of vinyl chloride in water, three important points should be considered:

- How strong are the complexes?
- What are the concentrations of the metal species?
- What are the concentrations of the competing ligands?

A survey of the literature did not disclose any equilibrium constants for the formation of coordinate complexes between vinyl chloride and metal ions. However, data for the formation of complexes between structurally related olefinic compounds and Ag^+ and Cu^+ (Table 3) indicate that electron-withdrawing groups attached to the double-bonded carbon atom of the olefin decrease the equilibrium constant. Assuming a concentration of 10 mg l^{-1} for the silver-ethylene complex, equilibrium calculations show the complex to be greater than 99% dissociated. Similarly, the cuprous- β -chloro-allyl alcohol complex at 6.2 mg l^{-1} is also greater than 99% dissociated. The effect of other ligands common to the aquatic environment, which would be competing for the metal ions, are neglected in these calculations. Thus we conclude that at low metal ion and vinyl chloride ion concentrations, complexation by these metal ions is not important.

Table 3. EQUILIBRIUM CONSTANTS FOR SOME COMPOUNDS
STRUCTURALLY RELATED TO VINYL CHLORIDE^a

Olefin (L)	Metal (M)	log k
Ethylene	Ag ⁺	1.93 ^b
Trans-dichloroethylene	Ag ⁺	-0.509 ^c
Cis-dichloroethylene	Ag ⁺	-0.796 ^c
Allyl alcohol	Ag ⁺	1.15 ^d
Allyl alcohol	Cu ⁺	4.72 ^e
β -chloroallyl alcohol	Cu ⁺	1.34 ^e

^a

$$K = \frac{(ML_n)}{(ML_{n-1})L} \quad , \text{ where } L_n = \text{number of ligands present.}$$

^bReference 22.

^cReference 23.

^dReference 24.

^eReference 25.

SECTION V

PHOTOCHEMICAL INTERACTIONS

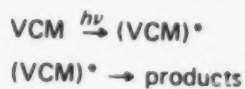
Several possible mechanisms exist for the decomposition of vinyl chloride by light (Figure 23). Mechanism I, direct photolysis, involves direct absorption of light by vinyl chloride followed by reaction from its excited state (VCM)*. Several studies have indicated that vinyl chloride in the vapor phase decomposes when irradiated with very short wavelength ultraviolet light (< 200 nm) (20, 27, 28). The primary reaction processes are homolysis of the carbon-chlorine bond yielding a chlorine atom and elimination of molecular HCl. Twisting around the double bond, an undetectable reaction, may also occur.

Mechanism II, photosensitized reaction via energy transfer, involves absorption of light by a triplet sensitizer followed by energy transfer to vinyl chloride to form its first excited triplet state, (VCM)*. Studies by Bellas *et al.* (29), for example, indicated that photolysis of vinyl chloride can be sensitized in the vapor phase by mercury atoms. The authors concluded that in this case, the primary photochemical process for triplet VCM in the vapor phase involved elimination of molecular HCl. However, homolysis of the carbon-chlorine bond could not be ruled out by their data. In solution, the major photoreaction for triplet chlorinated olefins was found to involve twisting around the double bond (30).

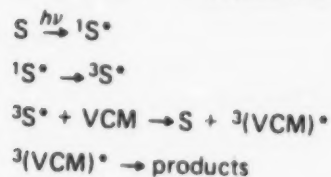
Mechanism III, which we have called chemical sensitization, involves direct chemical reaction between sensitizer and olefin. Such reactions are known to occur in the condensed phase with simple olefins and electronically excited ketones (31).

Mechanism IV, free radical decomposition and polymerization of VCM initiated by photochemical homolysis of a species like a peroxide, is also a possible pathway. Examples of the light-initiated polymerization of vinyl monomers are discussed by Walling (32). Uri and co-workers found that polymerization of vinyl monomers can be "photosensitized" by chlorophyll (33) and by iron complexes (34, 35). The "photosensitization" in these cases clearly did not involve energy transfer, but rather the generation of free radicals followed by polymerization (Mechanism IV).

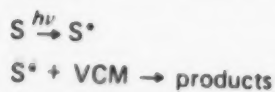
Mechanism I. Direct Photolysis



Mechanism II. Photosensitized Reaction (Energy Transfer)



Mechanism III. Chemical Sensitization



Mechanism IV. Light-initiated Free Radical Decomposition

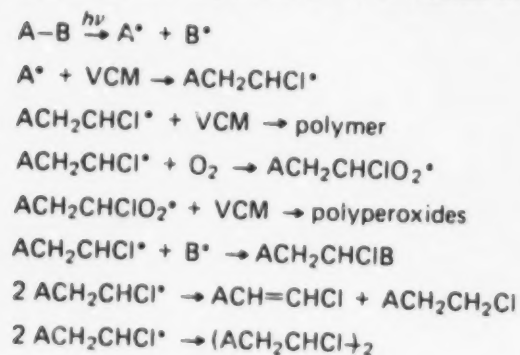


Figure 23. Pathways for light induced decomposition of vinyl chloride.

The photodegradation of vinyl chloride was studied to determine whether the above processes are possible in the aquatic environment, and whether their rates, if they occur, are sufficiently high to compete with other processes.

MATERIALS AND METHODS

Vinyl chloride gas from Matheson Company was used without further purification. Laboratory distilled water was redistilled from basic permanganate immediately prior to use.

Natural waters were obtained from the Oconee River in Athens, Georgia, and the Okefenokee Swamp (Big Water Lake) in South Georgia. Commercial humic acid was obtained from Aldrich Chemical Company.

Stock solutions of vinyl chloride were prepared in small bombs equipped with gas-tight Teflon stopcocks. Aliquants of VCM in gas-tight syringes were added to the bombs that were completely filled with known volumes of carbon tetrachloride; the gas rapidly dissolved into the CCl_4 . Aqueous solutions were prepared following the same procedures; the concentration in water was then measured exactly by comparison to the CCl_4 stock solutions. Analyses for VCM were performed by gas-liquid chromatography on a 2 m x 0.32 cm glass column packed with 0.4% Carbowax 1500 on Carbowax A. The column was cured by heating at 200°C for 48 hours with slow purging by nitrogen.

Glc analyses were performed on a Tracor MT-220 Chromatograph using a flame detector. Photolysis studies were conducted on a rotating turntable apparatus, described in detail by Moses, Liu, and Monroe (36). A 450-watt high-pressure mercury lamp was the light source. The ultraviolet spectrum of VCM in water was obtained with a Perkin-Elmer 602 Digital Spectrophotometer using a specially constructed quartz cell equipped with a gas-tight Teflon stopcock. All photolysis studies were carried out in reaction cells equipped with gas-tight Teflon stopcocks. Controls established that no leakage of VCM occurred from these cells over a period of at least two weeks.

Kinetic studies were generally carried out at VCM concentrations of 10 to 20 mg l^{-1} . The light from the mercury lamp was filtered through a 3 mm-thick Pyrex sleeve (cutoff at 300 nm) for most of the studies. Singlet oxygen

studies were conducted using 1.00×10^{-4} M methylene blue as sensitizer and 578 nm monochromatic light. Acetone sensitization studies employed 10% (by volume) acetone in water and 313 nm light. Filter solutions (1.0 cm thick) were as follows: 573 nm - 50 g cupric chloride (hydrated), 150 g anhydrous calcium chloride, and 150 g potassium dichromate in 500 ml distilled water slightly acidified by hydrochloric acid; 313 nm - 0.001 M potassium chromate in 3% aqueous potassium carbonate, and 3 nm-thick Pyrex sleeve. The actinometer for the acetone sensitized photolysis was a solution of 0.05 M benzophenone and 0.100 M cis-1,3-pentadiene in benzene (37).

RESULTS AND DISCUSSION

Direct Photolysis

The rate of direct photolysis of a pollutant is proportional to the degree of overlap between the electronic absorption spectrum of pollutant and the spectrum of light source, vinyl chloride and sunlight, respectively, for the present study. Atmospheric ozone prevents essentially all sunlight of wavelengths below 295 nm from reaching the earth's surface. Vinyl chloride, in the vapor phase, however, does not absorb above 220 nm (28), and our studies show that in water it does not absorb above 218 nm. The longer wavelength singlet-triplet transitions of simple ethylene derivatives that occur at wavelengths > 295 nm are highly forbidden and thus have extremely low extinction coefficients (38).

The lack of overlap between vinyl chloride absorption and sunlight radiation spectra indicates that direct photolysis of vinyl chloride would be very slow in the aquatic environment. To confirm this experimentally, we exposed solutions of vinyl chloride (10 mg l^{-1}) in pure water to filtered (> 300 nm) light from a mercury lamp. No photolysis occurred over a 90-hour period. The integrated intensity of the 300-370 nm light in our photochemical apparatus was found to be about eight times more intense than midday-June sunlight (lat. 34°N) in the same spectral region.

Indirect Photolysis

Although direct photolysis (Mechanism I) is immeasurably slow, the literature indicates that the light-induced transformations of vinyl chloride could occur through indirect pathways (Mechanisms II-IV). For example, substances found dissolved in certain natural waters were found to greatly accelerate the photodecomposition of some pesticides (39, 40). Photolysis experiments were therefore conducted in natural waters and in distilled water containing model photosensitizers that absorb light of wavelengths > 300 nm.

Vinyl chloride was not readily degraded by singlet oxygen, an excited form of oxygen generated by methylene blue photosensitization. However, in the presence of acetone, a high-energy triplet sensitizer, or hydrogen peroxide, a free radical source, VCM decomposed rapidly when irradiated with ultraviolet light. The disappearance quantum yield (313 nm) for the acetone-sensitized reaction (3.0×10^{-2} M VCM) was 0.75. A colorless precipitate formed during photolysis, but it was not identified.

Since the major photochemical process for triplet 1,2-dichloroethylene and other mono-olefins involves isomerization (30), twisting about its carbon-carbon bond would be expected to be the primary process for triplet VCM. Other studies have indicated that reaction between triplet ketones and olefins (41) to form oxetanes is not particularly efficient. Therefore the high disappearance quantum yield for the acetone-sensitized photolysis of VCM was surprising. The photolysis may involve inefficient homolysis of the carbon-chlorine bond of triplet VCM, followed by free-radical polymerization of VCM, i.e., most of the VCM would be consumed by secondary thermal reactions.

The importance of photosensitization via energy transfer for the disappearance of VCM in the environment is difficult to predict. Such sensitization occurs efficiently only when the triplet state energy of the sensitizer equals or exceeds that of the acceptor, i.e., VCM. Since the triplet state energies of mono-olefins are very high (78-82 kcal mole⁻¹) (38), only high energy sensitizers such as acetone (triplet energy 80 kcal mole⁻¹) are effective. Unfortunately, little is known about the concentrations and distribution of high-energy sensitizers in the aquatic environment. The matter is further complicated by the fact that competing energy acceptors such as dissolved oxygen are also present in the aquatic environment.

The high susceptibility of VCM to free radical attack in water was demonstrated by its rapid disappearance in the presence of hydroxy free radicals generated by photolysis of hydrogen peroxide (Figure 24). Since PVC plant effluents are likely to contain small amounts of peroxides, such as peroxydisulfate (32), that are used in the polymerization process, sunlight-induced decomposition of VCM was considered as a possible pathway for its disappearance from PVC plant effluent water.

However, using the same apparatus employed in the present direct photolysis studies, Thruston (3) found that VCM photolyzed very slowly (half-life 40 hours) in PVC plant effluent. When exposed to sunlight, it photolyzed even slower. Very little reaction was detected after 25 hours of exposure.

Our natural water studies were carried out in unfiltered waters collected from the Oconee River, a moderately polluted river in Athens, Georgia, and from the Okefenokee Swamp, an unpolluted water that is highly colored by dissolved humic materials. In both natural waters, and in water containing 20 mg l⁻¹ commercial "humic acid" (a derivative of decayed plants), no decomposition of VCM (10 mg l⁻¹) occurred during a 20-hour irradiation period.

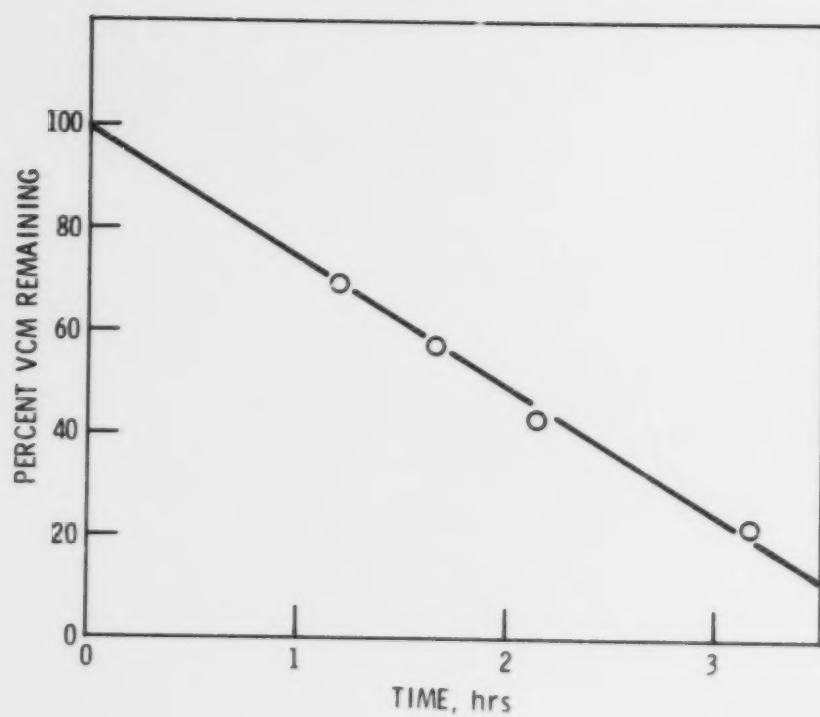


Figure 24. Decomposition of vinyl chloride in water by attack of free radicals generated by photolysis (300 nm) of hydrogen peroxide.

SECTION VI

MICROBIOLOGICAL INTERACTIONS

In natural waters, the interactions of vinyl chloride with living organisms must also be considered as a possible mechanism for disappearance of the compound. Two possible pathways were considered---sorption to microorganisms and degradation by bacteria. The toxicity of the vinyl chloride to bacteria was also investigated.

MATERIALS AND METHODS

Five mixed bacterial populations, three mixed fungal populations, and two single organism cultures (Bacillus subtilis, and Flavobacterium harrisonii) were isolated from natural aquatic systems in and near Athens, Georgia. An alga, Chlorella pyrenoidosa, was obtained from the Starr Collection, University of Indiana, Bloomington, Indiana.

A saturated solution of vinyl chloride was prepared by bubbling the gas into sterile distilled water for one hour. Vinyl chloride solutions for the bacterial degradation and toxicity studies were prepared by aseptically diluting the saturated solution to varying extents with a solution of nutrient broth that was diluted 1:20, 1:40, 1:80, or 1:100 in basal salts medium (42). The pH of the medium was 6.9. For the sorption studies, the saturated VCM solution was diluted with distilled water.

Analyses for VCM were done by direct gas-liquid chromatography (glc) using a Tracor MT-220 Chromatograph equipped with dual flame ionization detectors. Peak areas were obtained using a Varian Aerograph Model 477 integrator. VCM amounts were determined by comparison of glc peak areas from the experimental solutions with those from VCM gas standards in air prepared by MG Scientific Company. VCM eluted in approximately two minutes as a single, sharp symmetrical peak from a 1.5 meter Porapak Q (Waters Associates, Inc.) column (4 mm ID) at an oven temperature of 125°C, an injection port temperature of 215°C, and a carrier gas (nitrogen) flow rate of 90 ml/min.

For the degradation and toxicity studies, 250-ml flasks with side arms and screw caps, as illustrated in Figure 25,

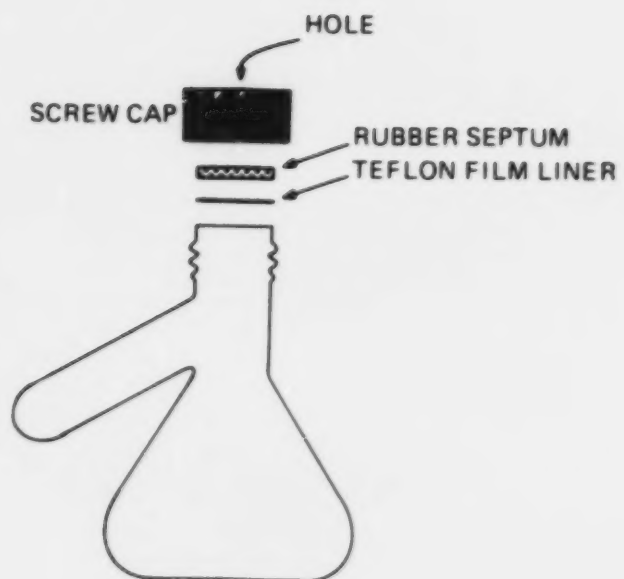


Figure 25. Apparatus for vinyl chloride degradation and toxicity studies.

were used. The VCM stock solution was introduced by syringe through the hole in the screw top into flasks containing dilute nutrient broth and bacteria. Samples for glc analysis were removed in the same manner. The Teflon liner covering the top was sealed with cellulose tape immediately after the syringe was removed.

The side-arm tube was designed to fit the Klett-Summerson photoelectric colorimeter in which turbidity of the culture was measured using a blue filter (425 nm). This allowed growth to be monitored without opening the flasks.

Each isolated bacterial population was inoculated into two flasks containing 1:20 nutrient broth. The saturated VCM solution was added to one of the cultures to give a final concentration of 20 mg VCM per liter. The other culture, the control, received no VCM. Each series of cultures included a flask containing medium and VCM but no organisms. The cultures were incubated at 21°C on a gyratory shaker under an exhaust hood.

After one week the resultant populations were transferred to a 1:20 nutrient broth solution containing 40 mg l⁻¹ VCM. Weekly transfers were made for a period of five weeks, decreasing the nutrient broth concentration and increasing the VCM concentration until nutrient broth was diluted 1:80 and VCM concentration was 120 mg l⁻¹. After five weeks, bacteria for degradation studies were harvested from the 1:80 nutrient broth containing 120 mg l⁻¹ VCM, washed three times, and transferred to basal salts medium containing 54 mg l⁻¹ VCM as the only carbon source. Inocula from the same series of flasks were used to continue the toxicity studies. The concentration of nutrient broth was decreased to a ratio of 1 part nutrient broth to 100 parts basal salts medium and the concentration of the vinyl chloride was increased at each 48-hour transfer until the VCM concentration was 900 mg l⁻¹.

Bacteria used in sorption studies were grown in 1:10 nutrient broth for 24 hours, harvested, and washed three times. Enough bacteria were transferred to 5-ml graduated centrifuge tubes with ground glass stoppers to give approximately 5 g dry weight of bacteria per liter of water.

Fungi from three field sites were isolated on Rose Bengal (Difco) plates and maintained on Sabouraud's medium (Difco) slants. Inocula for fungi were suspensions prepared by agitating 10 ml of sterile water in a plate containing the sporulating fungi. The suspension was introduced into

medium containing 6.0 g glucose per liter. Medium was decanted and enough fungi were transferred to 5-ml graduated centrifuge tubes with ground glass stoppers to give approximately 5 g dry weight of fungi per liter of water.

Chlorella pyrenoidosa was grown in Bensen-Fuller medium containing 0.1% Hutner's trace element solution and incubated on a shaker at 15°C under 170 ft-c of continuous light. Cultures were centrifuged, washed three times, and transferred to 5-ml graduated centrifuge tubes with ground glass stoppers for sorption studies to give approximately 4 g dry weight of algae per liter of water. To eliminate corrections for volatilization of VCM to the air above the solution, tubes were filled to the top and all data were compared with data from control tubes (containing no organisms).

To determine dry weights of algae and bacteria used in sorption studies, cultures were centrifuged and the organisms were washed three times. The organisms were quantitatively transferred to tared beakers and dried to a constant weight at 90°C. Fungi were separated from test cultures for dry weight determinations by filtering, first through tared pre-filters, then through tared 0.22 micron Nucleopore filters, and by drying to a constant weight at 90°C.

RESULTS AND DISCUSSION

Sorption of Vinyl Chloride to Microorganisms

In systems in which sorption is linear (very low solute concentrations), the simple distribution coefficient (K_d) may be used to describe the extent of sorption of a compound to microorganisms

$$K_d = \frac{x/m}{c_e} \quad (3)$$

where c_e = concentration (mg/mg) of solute in solution at equilibrium

x = amount (mg) of material sorbed per mg of solution ($c_0 - c_e$, where c_0 = initial concentration)

m = dry weight (mg) of microorganisms per liter

Experimentally, the quantity of vinyl chloride sorbed can be estimated as the difference between total VCM in the system (c_0) and that in the supernatant at equilibrium (c_e). The concentration of organisms (m) required to detect a K_d of 10 for a given c_0 of 25 mg VCM/l can be determined from equation (3) by assuming a K_d of 10 and a value for c_e slightly greater than the experimental error involved in VCM determinations. Concentrations of microorganisms calculated to give $K_d \geq 10$ were used in our experiments and supernatants were sampled at 30 minutes, 24 hours, and 48 hours.

Vinyl chloride did not sorb to a detectable extent to any of the organisms tested---the five bacterial populations, *B. subtilis*, *E. harrisonii*, the three fungal populations, or *Chlorella pyrenoidosa*; the distribution coefficients for all organisms were therefore less than 10.

In previous studies in our laboratory, the degree of sorption of various pesticides to microorganisms was found to correlate inversely with the water solubility of the pesticides. The more water soluble compounds (malathion, diazinon, parathion, and carbaryl) did not sorb to any detectable extent, whereas the less water soluble compounds (methoxychlor and toxaphene) did sorb. Since vinyl chloride is more water soluble than the above insoluble pesticides, its inability to sorb to the microorganisms would therefore be expected.

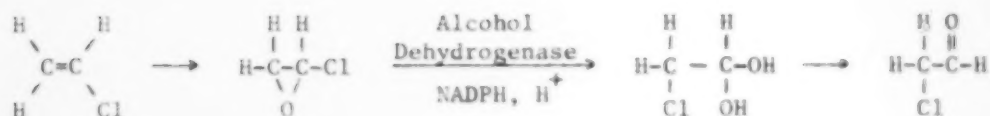
Bacterial Degradation

Only mixed bacterial populations were used in the degradation studies since they often show a greater facility to acclimate than a single species culture.

The test cultures were monitored for decrease in VCM concentration by direct injection of the aqueous culture (organisms and media) into the glc. Nutrient broth concentration was decreased and VCM concentration was increased at each transfer. VCM concentration was monitored for 20 hours between transfers. No change in concentration was detected at any VCM level. At the end of this period the bacterial populations were transferred to medium

containing only basal salts and 54 mg l⁻¹ VCM without an additional carbon source. These cultures were monitored daily for one week. No degradation was detected at any time in any of the cultures.

Byington and Liebman (43) have shown that trichloroethylene was transformed to chloral hydrate by rat, rabbit, and dog liver microsomes in a reaction requiring NADPH and oxygen. Based on the structures of the compounds and the requirement of NADPH, alcohol dehydrogenase may be the active enzyme. If so, degradation of VCM by bacteria could be possible via the following pathway:



If the bacteria were capable of degrading VCM by this pathway, a system in which oxygen was not a limiting factor would be needed. The closed flask systems described earlier could limit the oxygen in the system. Therefore, six one-liter flasks containing the five bacterial populations in 1:40 nutrient broth and an uninoculated control were bubbled with 0.1% VCM in air for 96 hours and monitored for possible products by glc analysis at low column temperature using FID. No degradation products were detected in any of the cultures.

Toxicity of Vinyl Chloride to Bacteria

The toxicity of VCM to five actively growing bacterial populations was tested. Testing could not be done at VCM concentrations up to its solubility in water (1700 mg l⁻¹) because of the difficulty in supplying the bacteria with sufficient oxygen for growth above a VCM concentration of 900 mg l⁻¹. Because even at 900 mg l⁻¹ VCM the oxygen concentration was low, a low nutrient broth concentration was used also (1:100) to insure that any differences in growth would be due to the presence of VCM rather than insufficient oxygen. No difference could be detected between bacterial growth in cultures and in test cultures containing up to 900 mg l⁻¹ VCM. The VCM was therefore not toxic to bacteria at these concentrations.

SECTION VII

PHYSICAL INTERACTIONS

The conceptual model for vinyl chloride behavior in aquatic systems suggests that volatilization may be an important process in determining the distribution of the compound. A preliminary study of the stability of vinyl chloride in water (3) indicates that the loss of vinyl chloride from water through volatilization is relatively rapid. Gas exchange experiments were therefore undertaken to provide data for determination of the specific rate of volatilization of vinyl chloride from water.

The specific rate of gas exchange (K) at an interface between water and atmosphere is a function of properties (P) of the gas molecules (e.g., diffusivity, molecular diameter), and the turbulence (T) in the water,

$$K = f(P,T) \quad (4)$$

If the specific rates are determined from concentrations measured for two gases (denoted 1 and 2) simultaneously, the common parameter, turbulence, can be eliminated from the functional relationship

$$\frac{K_1}{K_2} = \frac{f(P_1,T)}{f(P_2,T)} = \text{constant} \quad (5)$$

for constant properties P_1 and P_2 . This ratio (equation 5) of specific rates is not significantly affected by temperature changes between 10°C and 30°C, by the level of turbulence, by the direction of gas transfer, or by the presence of dissolved solids (8). In the gas exchange experiments, the specific rate of vinyl chloride loss was determined relative to and concurrently with the specific

rate of oxygen re-aeration to eliminate the need for measurement of turbulence and to relate vinyl chloride volatilization to available environmental determinations of oxygen re-aeration.

For comparison, the ratio of specific rates was also calculated using estimates of molecular diameter.

MATERIALS AND METHODS

Nitrogen-sparged, deionized water (900 ml) and saturated vinyl chloride solution (10 ml) were added to each of four beakers in an exhaust hood. The contents of beakers 1, 2, 3, and 4 were stirred to create vortices with depths of 0 (quiescent), 1.5 cm, 5 cm, and 10 cm, respectively. Oxygen and vinyl chloride concentrations were measured every 10 minutes for 180 minutes using a dissolved-oxygen meter and a gas chromatograph. Six replications of these experiments were performed.

RESULTS AND DISCUSSION

The gas exchange dynamics at the interface were represented as a first-order approach to equilibrium using the equation

$$\frac{dC}{dt} = K(C_s - C) \quad (6)$$

where C = gas concentration
 t = time
 K = specific rate
 C_s = saturation concentration

The concentrations of oxygen and vinyl chloride for each beaker in each replicate were used to determine the sums of squares for the best least squares fit to the logarithmic form of the solution to equation 6. The corrected sums of squares for all beakers stirred alike were pooled to

estimate the specific rates for each of the four levels of mixing. These specific rates are presented in Table 4 with their 95% confidence intervals. A linear regression of K_{VCM} on K_{O_2} resulted in the equation

$$K_{VCM} = 2.30 K_{O_2} \quad (7)$$

giving a constant ratio of

$$\frac{K_{VCM}}{K_{O_2}} = 2.30 \pm 0.31 \quad (8)$$

at a 95% level of confidence. The constant ratio line and ratios at each mixing level are graphed in Figure 26.

The ratio of gas exchange coefficients may also be estimated as the reciprocal of the ratio of molecular diameters (9). Two different values for the vinyl chloride diameter may be obtained depending upon the method by which it is calculated. The diameter calculated using a critical volume of 168.9 ml mole⁻¹ (44) in the van der Waals equation is 3.55 Å. Assuming a molecular diameter for oxygen of 2.95 Å, the resulting ratios of gas exchange coefficients using the two different diameters are

$$\frac{K_{VCM}}{K_{O_2}} = 0.83 \text{ and } 0.87 \quad (9)$$

respectively.

The experimentally determined estimate of the ratio of gas exchange coefficients (K_{VCM}/K_{O_2}) indicates that the

**Table 4. RATE COEFFICIENTS FOR OXYGEN AND VINYL CHLORIDE
GAS EXCHANGE AT FOUR MIXING LEVELS**

Vortex depth (cm)	K_{O_2} (min^{-1})	K_{VCM} (min^{-1})
0	$-3.54(10^{-3}) \pm 2.28(10^{-4})$	$-3.03(10^{-3}) \pm 2.74(10^{-4})$
1.5	$-1.24(10^{-2}) \pm 1.45(10^{-3})$	$-1.29(10^{-2}) \pm 1.22(10^{-3})$
5.0	$-3.85(10^{-2}) \pm 1.16(10^{-2})$	$-8.19(10^{-2}) \pm 1.06(10^{-3})$
10.0	$-8.03(10^{-2}) \pm 3.86(10^{-2})$	$-1.75(10^{-1}) \pm 7.88(10^{-2})$

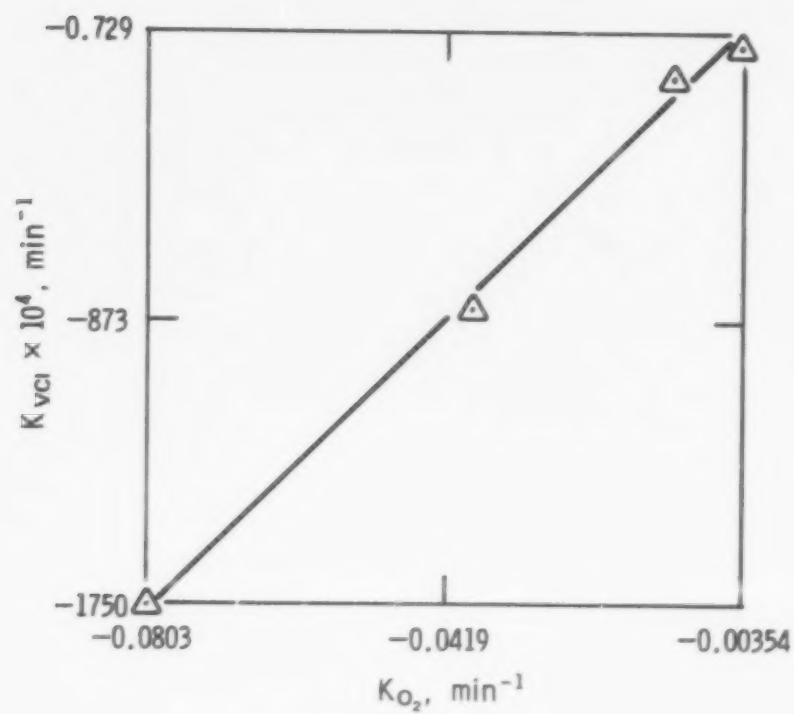


Figure 26. K_{VCI} versus K_{O_2} at four mixing levels.

specific rate of exchange of vinyl chloride gas between water and air is about twice that of oxygen.

REFERENCES

1. U. S. Environmental Protection Agency. Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, Kentucky. Surveillance and Analysis Division, Athens, Georgia. June 1974. 45p.
2. Gillett, J. W., J. Hill, IV, A. W. Jarvinen, and W. P. Schoor. A Conceptual Model for the Movement of Pesticides Through the Environment. National Environmental Research Center, Corvallis, Oregon. EPA-660/2-74-024. December, 1974. 80p.
3. Thruston, A. D., Jr. and A. W. Garrison. Stability of Vinyl Chloride Monomer in Water. Internal Report, Southeast Environmental Research Laboratory, Athens, Georgia. 1974. 2p.
4. Director, S. W. and M. A. Rohrer. Introduction to System Theory. New York, McGraw Hill, Inc., 1972. 441p.
5. Tsivoglou, E. C. and J. K. Wallace. Characterization of Stream Reaeration Capacity. Georgia Institute of Technology. Office of Research and Monitoring, Washington, D. C. EPA-R3-72-012. October, 1972. 315p.
6. Baca, R. G., M. W. Lorenzen, R. D. Mudd, and L. V. Kimmel. A Generalized Water Quality Model for Eutrophic Lakes and Reservoirs. Pacific Northwest Laboratories. Richland, Washington. 211801602. Office of Research and Monitoring, U. S. Environmental Protection Agency. August, 1974. 140p.
7. Hutchinson, G. E. A Treatise on Limnology. Volume I. New York, John Wiley and Sons, Inc., 1957. 1015p.
8. Russell-Hunter, W. D. Aquatic Productivity. Toronto, Collier Macmillan, 1970. 305p.
9. Tsivoglou, E. C. Tracer Measurement of Stream Reaeration. Georgia Institute of Technology. Washington, D. C. Water Pollution Control Administration. June, 1967. 86p.

10. Martens, H. R. and D. R. Allen. Introduction to Systems Theory. Columbus, Ohio, Charles E. Merrill Books, Inc., 1969. 611p.
11. Giorgio Modena. Accounts Chem. Res. 4:73, 1971.
12. Cockerill, A. F. In: Comprehensive Chemical Kinetics, Volume 9, Bamford, C. H. and C. F. H. Tipper (eds.). New York, American Elsevier Scientific Publishing Co., Inc., 1973. p. 163.
13. Bolton, R. In: Comprehensive Chemical Kinetics, Volume 9, Bamford, C. H. and C. F. H. Tipper (eds.). New York, American Elsevier Scientific Publishing Co., Inc., 1973. p. 1.
14. Walling, C. Free Radicals in Solution. New York, John Wiley and Sons, Inc., 1957. p. 397
15. Rappoport, Z. and A. Gal. J. Am. Chem. Soc. 91:5246, 1969.
16. Kalinin, A. I., E. M. Perepletchikova, I. A. Korshunov, and E. N. Zil'berman. Zh. Obshch. Khim. 36:1563, 1966. C. A. 66:61277C.
17. Miller, S. I. J. Org. Chem. 26:2619, 1961.
18. Jones, D. E., R. O. Morris, C. A. Vernon, and R. P. M. White. J. Chem. Soc. 2349, 1960.
19. Ehnerson, S., S. Seltzer, and R. Dufferback. J. Am. Chem. Soc. 87:563, 1965.
20. Shelton, J. R. and L. H. Lee. J. Org. Chem. 25:428, 1960.
21. Israel, G. C., J. K. Martin, and F. G. Soper. J. Chem. Soc. 1282, 1950.
22. Brandt, P. Acta Chem. Scand. 13:1639, 1959.
23. Andrews, L. J. and R. M. Keefer. J. Amer. Chem. Soc. 73:5733, 1951.
24. Winstein, S. and H. J. Lucas. J. Amer. Chem. Soc. 60:836, 1938.

25. Keefer, R. M., L. J. Andrews, and R. E. Kepner. J. Amer. Chem. Soc. 71:3906, 1949.
26. Rennert, A. M. Diss. Abstr. B, 29:1630, 1968.
27. Ausloos, P., R. E. Rebbert, M. H. J. Wijnen. J. Res. Nat. Bur. Stand. Sec. A, 77:243, 1973.
28. Fijimoto, T., A. M. Rennert, M. H. J. Wijnen. Ber. Bunsenges. Phys. Chem. 74:282, 1970.
29. Bellan, M. G., J. K. S. Wan, W. F. Allen, O. P. Strausz, and H. Grunning. J. Phys. Chem. 68:2170, 1964.
30. Hammond, G. S., N. J. Turro, and P. A. Leermakers. J. Phys. Chem. 66:1144, 1962.
31. Arnold, D. R. Advan. Photochem. 6:301, 1968.
32. Walling, C. Free Radicals in Solution. New York, John Wiley and Sons., Inc., 1957. p. 179.
33. Uri, N. J. Amer. Chem. Soc. 74:5808, 1952.
34. Evans, M. C. and N. Uri. Nature. 164:404, 1949.
35. Evans, M. G., M. Santappa, and N. Uri. J. Polymer Sci. 7:243, 1951.
36. Moses, P. G., R. S. H. Liu, and B. M. Monroe. Mol. Photochem. 1:245, 1969.
37. Lamola, A. A. and G. S. Hammond. J. Chem Phys. 41:2129, 1965.
38. Merer, A. J. and R. S. Mulliken. Chem. Rev. 69:639, 1969.
39. Zepp, R. G., N. L. Wolfe, and G. L. Baughman. Southeast Environmental Research Laboratory, Athens, Georgia. (Presented in part at the 168th National Meeting of the American Chemical Society. Atlantic City. September, 1974.)
40. Ross, R. D. and D. C. Crosby. J. Agr. Food Chem. 21:335, 1973.
41. Wagner, P. J. and I. H. Kochewan. J. Amer. Chem. Soc. 92:5742, 1970.

42. Payne, W. J. and V. E. Feisal. *Appl. Microbiol.* **11**:339-344, 1963.
43. Byington, K. H. and K. C. Leibman. *Mol. Pharmacol.* **1**(3):247-254, 1965. *C. A.* **64**:11457e, 1966.
44. Dreisback, R. R. *Physical Properties of Chemical Compounds. Advances in Chemistry Series, Numbers 15, 22, and 29.* Washington, D. C., American Chemical Society, 1955-1961. 407p.
45. Veast, R. C. (ed). *Handbook of Chemistry and Physics.* Cleveland, Ohio, Chemical Rubber Co., 1971. p. F173-F177.